H. CLARK

SOLID STATE PHYSICS

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an introduction to its theory

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Preface

This book is intended to be a realistic introduction to the theory of solid state physics. It is meant to fill the gap between the more empirical books such as Kittel's *Introduction to Solid State Physics* or Dekker's *Solid State Physics*, and the more advanced theoretical texts such as Kittel's *Quantum Theory of Solids*. No claim is made that the subject is covered comprehensively. This is clearly not possible within a book of this size. However, it is hoped that the included material will give a good basic background to the subject.

This text should be useful to research workers both in industry and university, and to final honours students. It should be especially appropriate to the several new M.Sc. courses in *Solid State Physics*. The reader is assumed to have taken a first course in Quantum Mechanics.

Problems are included at the end of each chapter and a few of these have been used to extend the theory slightly. M.K.S. (Sommerfeld) units are used throughout and the charge on the electron is taken as $-e = -1 \cdot 602 \times 10^{-19}$ C.

H. C.

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The One-electron Approximation

§ 1.1 The quantum mechanics

When it is noted that the interatomic distance in solids is of the order of a few angstrom units, it is not at all obvious how it is possible to separate the motion of the electrons in any sense. This monograph is primarily concerned with the results obtainable from the one-electron approximation and it is the purpose of the first chapter to indicate the relevant theoretical background. Initially it is necessary to explain how the motion of the electrons can be treated apart from the lattice of heavy ions and then to deal with the separation of the electrons themselves.

The results of the Schrödinger wave mechanics will be used freely throughout this book and perhaps it is as well to recount briefly the main results of quantum mechanics. For further information the reader is referred to any of the standard texts such as Schiff or Mandl.

In quantum theory, the state of any physical system is described as completely as possible by a wave function ψ which in general is complex and depends on the position co-ordinates of all the N particles and on the time. Strictly ψ depends upon the spin co-ordinates as well. This will be emphasized where appropriate.

The real quantity $\psi^*\psi d\tau$ is the probability that the co-ordinates q_i of the particles lie within the volume element

$$d\tau = dq_1 dq_2 \ldots dq_{3N}$$

at the time t.

To be physically meaningful, the wave functions must be single-valued and in general they are continuous and quadratically integrable. The latter property makes it possible to normalize the wave function to unity,

i.e. $$\int \psi^* \psi d\tau = 1$$

The physical observables like energy and angular momentum which are present in classical theory in the form of dynamical variables are represented in quantum mechanics by operators which are both linear and Hermitian. A linear operator A has the property

$$A(a\psi_1 + b\psi_2) = aA\psi_1 + bA\psi_2 \qquad (1.1)$$

where ψ_1, ψ_2 are two state functions and a, b are constants. The Hermitian condition demands that

$$\int \psi_1^* A\psi_2 d\tau = \left(\int \psi_2^* A\psi_1 d\tau \right)^* \qquad (1.2)$$

There are some general rules to act as a guide in finding the form for these operators. In the Schrödinger representation they are:

(i) the operator representing one of the position co-ordinates q_i or the time t is simply q_i or t.

(ii) the operator representing one of the components of momentum p_i conjugate to q_i is $\dfrac{\hbar}{i} \dfrac{\partial}{\partial q_i}$.

The quantum operator representing a dynamical variable which is expressed in terms of the position co-ordinates, momentum and time is obtained by substitution using the above rules.

As an example consider the angular momentum of a point mass moving in some orbit. Classically the angular momentum

L of such a particle about an axis through the origin is given by the vector product

$$L = r \wedge p$$

where *r* is the radius vector and *p* the momentum of the particle. For a particle moving in the *x–y* plane the angular momentum vector lies along the *z*-axis and

$$L_z = xp_y - yp_x$$

The quantum mechanical operator which represents the angular momentum is

$$\mathscr{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

If the state function ψ is an eigenfunction of the operator A corresponding to a classical variable,

i.e. $$A\psi = a\psi \qquad (1.3)$$

where *a* is some constant, then in this state the variable has precisely the value *a*. *a* is an eigenvalue. It can be shown that the eigenvalues of a Hermitian operator are real and that if ψ_i and ψ_j are eigenfunctions belonging to different eigenvalues then they are orthogonal,

i.e. $$\int \psi_i^* \psi_j d\tau = 0 \quad i \neq j$$

Two operators A and B are said to commute if

$$(AB)\psi = (BA)\psi$$

when applied to an arbitrary wave function ψ. Quantum mechanical operators do not always possess this property. The operators representing the position co-ordinate *x* and the conjugate momentum p_x do not commute,

i.e. $$\frac{\hbar}{i}\left(\frac{\partial}{\partial x}x - x\frac{\partial}{\partial x}\right)\psi = \frac{\hbar}{i}\psi$$

When two operators commute it can be shown that there exists a set of functions which are simultaneously eigenfunctions for

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both operators. This result is important in the classification of states and is referred to again in Chapter 3.

In classical mechanics the Hamiltonian H defines the total energy for a conservative system. The time variation of the state is determined through Hamilton's equations. The most important quantum mechanical operator is the analogous Hamiltonian $\mathscr{H}$ obtained by substitution. The dependence of the state function ψ on the time is given by

$$\mathscr{H}\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t} \qquad (1.4)$$

This is the time-dependent Schrödinger equation.

If ψ is an eigenfunction of the Hamiltonian operator, the eigenvalue gives the energy E of the state and the wave function merely changes its phase in time,

i.e. $\qquad\qquad \mathscr{H}\psi = E\psi \qquad\qquad (1.5)$

and $\qquad\qquad \psi_t(E) = \psi_0(E)e^{-iEt/\hbar} \qquad (1.6)$

Equation (1.5) is the time-independent Schrödinger equation. In an eigenstate of the energy, the average value of any observable A, defined by

$$\int \psi^* A\psi \mathrm{d}\tau$$

is a constant if A does not explicitly involve the time. The wave function is then said to define a stationary state.

For those readers completely new to solid state theory it is possible to omit the remainder of this chapter on a first reading.

§ 1.2 The Born–Oppenheimer approximation

The classical Hamiltonian for a collection of N particles of masses m_i and charges e_i respectively, is given by

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{\substack{i=1 \\ (i \neq j)}}^{N}\sum_{j=1}^{N}\frac{e_ie_j}{4\pi\epsilon_0\,|r_i - r_j|} \qquad (1.7)$$

where r_i is the position vector of the ith particle. The first sum

is taken over the $3N$ components of momenta and represents the kinetic energy of the system. The second term represents the electrostatic potential energy of the system and the sum is over all the possible pairs of particles. The corresponding quantum mechanical Hamiltonian is (omitting spin-dependent terms),

$$\mathscr{H} = \sum_i \left(\frac{-\hbar^2}{2m}\right)\nabla_i{}^2 + \frac{1}{2}\sum_{i \neq j} \sum_j \frac{e_i e_j}{4\pi\epsilon_0 \,|r_i - r_j|} \qquad (1.8)$$

where $\nabla_i{}^2$ operates on the spatial co-ordinates of the ith particle. The eigenfunctions of this operator must involve the $3N$ position co-ordinates of the system ($4N$ if spin is included).

In a crystal there are two types of particles present, the nuclei and the electrons. For our purpose the structure of the nucleus may be ignored.

The Schrödinger equation for a stationary state of a crystal may be written

$$\mathscr{H}(R_1, R_2, \ldots; r_1, r_2, \ldots)\, \Psi\,(R_1, R_2, \ldots; r_1, r_2, \ldots)$$
$$= E_t\, \Psi\,(R_1, R_2, \ldots; r_1, r_2, \ldots) \qquad (1.9)$$

where the wave function Ψ and the Hamiltonian are functions of all the nucleus and electron co-ordinates R_i and r_i respectively. The number of variables is reduced if the atomic electrons are separated into core and valence electrons, although this division is somewhat arbitrary. The core electrons have atomic wave functions which do not overlap to any appreciable extent at the observed interatomic spacing in the crystal and consequently may be considered to be unaffected by combining the atoms to form a crystal. Conversely, the wave functions of the valence electrons overlap considerably, and are modified by the process of crystal formation.

The Hamiltonian of (1.9) then contains all the interactions of an assembly of ion cores and valence electrons and may be expressed as

$$\mathscr{H}(R_1, R_2 \ldots; r_1, r_2, \ldots)$$
$$= \mathscr{H}_{\text{ion}}(R_1, R_2, \ldots) + \mathscr{H}_{\text{electron}}(r_1, r_2, \ldots)$$
$$+ \mathscr{H}_{\substack{\text{electron} \\ \text{-ion}}}(R_1, R_2, \ldots; r_1, r_2, \ldots) \qquad (1.10)$$

where
$$\mathscr{H}_{\text{ion}} = -\sum_i \frac{\hbar^2}{2M}\nabla_{R_i}^2 + \frac{1}{2}\sum_i\sum_{i\neq j}W(R_i - R_j)$$

$$\mathscr{H}_{\text{electron}} = -\sum_i \frac{\hbar^2}{2m}\nabla_{r_i}^2 + \frac{1}{2}\sum_i\sum_{i\neq j}\frac{e^2}{4\pi\epsilon_0\,|r_i - r_j|}$$

and
$$\mathscr{H}_{\substack{\text{electron}\\\text{-ion}}} = \sum_i\sum_j v\,(r_i - R_j)$$

The ionic Hamiltonian $\mathscr{H}_{\text{ion}}$ describes the motion of the set of like ions, each composed of a nucleus and a shell of core electrons, which interact through a potential $W(R_i - R_j)$. $\mathscr{H}_{\text{electron}}$ corresponds to the valence electrons which interact through a Coulomb potential. The electron-ion Hamiltonian takes account of the interaction between the ionic cores and valence electrons which are assumed to act through a potential $v(r_i - R_j)$.

The total crystal potential may be written

$$V_c = V_{\text{ion}} + V(R_1, R_2, \ldots; r_1, r_2, \ldots)$$

with

$$V_{\text{ion}} = \tfrac{1}{2}\sum_{i\neq j}\sum W(R_i - R_j)$$

$$V = \tfrac{1}{2}\sum_{i\neq j}\sum \frac{e^2}{4\pi\epsilon_0\,|r_i - r_j|} + \sum_i\sum_j v(r_i - R_j)$$

where V_{ion} is the potential of interaction between the ion cores, and V is the potential of interaction of the electrons with the ion cores and with each other.

Because the electronic masses are much less than the ionic masses, the electrons move much more rapidly than the ions. In the 'Born–Oppenheimer' approximation (1927), the Schrödinger equation is solved for the N electrons in the field of all the ions in some fixed configuration. The electronic wave function $\psi(R_1, R_2, \ldots; r_1, r_2, \ldots)$ depends on the variable positions of the electrons r_i and also on the nuclei-co-ordinates R_i regarded as parameters. The full crystal wave function is written

$$\begin{aligned}\Psi(R_1, R_2, \ldots; r_1, r_2, \ldots) = {}& \Phi(R_1, R_2, \ldots)\,.\\ & \psi(R_1, R_2, \ldots; r_1, r_2, \ldots)\end{aligned} \quad (1.11)$$

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where Φ is the lattice wave function describing the ionic motion and is a function of the co-ordinates R_i only.

ψ satisfies the equation,

$$\left[-\sum_i \frac{\hbar^2}{2m} \nabla_{r_i}^2 \right.$$
$$\left. + V(R_1, R_2, \ldots; r_1, r_2, \ldots) \right] \psi(R_1, R_2, \ldots; r_1, r_2, \ldots)$$
$$= E(R_1, R_2, \ldots) \psi(R_1, R_2, \ldots; r_1, r_2, \ldots) \quad (1.12)$$

where m is the electron mass and $\nabla_{r_i}^2$ operates on the electron co-ordinates. The electron energy eigenvalue $E(R_1, R_2, \ldots)$ depends upon the particular ionic configuration considered. This electron energy then appears as part of the effective potential for the nuclear motion.

$$\left\{ -\sum_j \frac{\hbar^2}{2M} \nabla_{R_j}^2 + [V_{\text{ion}}(R_1, R_2, \ldots) \right.$$
$$\left. + E(R_1, R_2, \ldots)] \right\} \Phi(R_1, R_2, \ldots)$$
$$= E_L \Phi(R_1, R_2, \ldots) \quad (1.13)$$

The error produced by using the Born–Oppenheimer approximation is small when the characteristic frequencies of vibration of the ions are much smaller than the characteristic electronic frequencies. Generally this implies that the ionic mass may be much greater than the electronic mass which is, of course, correct. However, if the energy required to excite an electron to a higher level is small, implying a small electronic frequency, the approximation breaks down. This is the case for metals and then the ionic function Φ depends on the electron co-ordinates as well as the ionic co-ordinates.

Equation (1.12) describes the electronic motion in a static lattice. In practice it is solved assuming both the crystal symmetry and the lattice constant. This implies that the electronic potential is a function of the electron co-ordinates only, and so the electron energy cannot be used in (1.13) to determine the nuclear motion. The equation becomes

$$\left[-\sum_i \frac{\hbar^2}{2m} \nabla_{r_i}^2 + V(r_1, r_2, \ldots) \right] \psi(r_1, r_2, \ldots)$$
$$= E\psi(r_1, r_2, \ldots) \quad (1.14)$$

the atomic co-ordinates being given their observed mean values. The potential includes all the interactions involving the valence electrons and can be written

$$V(r_1, r_2, \ldots) = \sum_i V_L(r_i) + V_e(r_1, r_2, \ldots)$$

where $V_L(r_i)$ represents the interaction between the ith electron and the ion cores and where V_e represents the total electron–electron interaction.

§ 1.3 One-electron approximation

It is extremely difficult to solve atomic or nuclear problems involving more than one electron. Even in the simplest cases complicated numerical procedures have proved necessary. The difficulty arises because the electron–electron potential contains terms of the form $e^2/4\pi\epsilon_0 \mid r_i - r_j \mid$ involving the spacial co-ordinates of two electrons. In the one-electron formulations approximate solutions which treat the electrons separately are considered. The Hartree method employs a simple product wave function of the form

$$\psi(r_1, \ldots r_N) = \phi_1(r_1)\phi_2(r_2) \ldots \phi_N(r_N) \quad (1.15)$$

It is important that the one-electron functions be normalizable and that there be as many as electrons present. For the ground state, the variational theorem of quantum mechanics requires that the expectation value of the energy be a minimum. Consequently, the best Hartree solution is that which minimizes the integral

$$\int \psi^*(r_1, \ldots, r_N) \mathscr{H} \psi(r_1, \ldots, r_N) d\tau \quad (1.16)$$

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where $\mathscr{H}$ is the Hamiltonian of equation (1.14), subject to the restrictive conditions

$$\int \phi_i^*(r_1)\phi_i(r_1)d\tau_1 = 1 \qquad (1.17)$$

This procedure may be carried out by the method of Lagrange multipliers and the one-electron wave functions which minimize (1.16) and satisfy (1.17) are given by

$$\mathscr{H}_i \phi_i(r_1) = E_i \phi_i(r_1) \qquad (1.18)$$

where $\mathscr{H}_i$ is the one-electron Hamiltonian.

$$\mathscr{H}_i = -\frac{\hbar^2}{2m}\nabla_1^2 + V_L(r_1)$$
$$+ e^2\sum_j{}' \int \frac{\phi_j^*(r_2)\phi_j(r_2)}{4\pi\epsilon_0 |r_1 - r_2|}d\tau_2 \qquad (1.19)$$

The summation in the final term is over all the one-electron wave functions except the ith. Each term may be given a physical significance. The first term represents the kinetic energy of the first electron, the second term represents the interaction between the electron and the ion cores and the final term represents the average Coulomb energy of the electron in the field produced by all the other electrons.

The Hamiltonian is not identical for all electrons and the eigenfunctions are not orthogonal.

The simple Hartree method does not entirely neglect the influence of one electron upon another. Each electron moves in the average field of the remainder. However, there is a serious fault in the Hartree wave function. In quantum mechanics it is impossible to distinguish between identical particles. This means that if any two electrons are interchanged the initial and final states of the system must have identical physical properties. Consequently the wave function can only change by an unimportant phase factor. If the operator P_{ik} interchanges the co-ordinates (including spin) of the ith and kth electrons then

$$P_{ik}\psi = e^{i\delta}\psi$$

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By repeating this interchange the original wave function is restored. Hence it follows that $e^{i2\delta} = 1$ or $e^{i\delta} = \pm 1$,

i.e. $$P_{ik}\psi = \pm \psi$$

The wave function is either symmetric or antisymmetric with respect to permutations of the electron co-ordinates, when spin is included. Experimental evidence (Pauli principle) shows that electrons, and in fact all particles with half-integral spin, have antisymmetric wave functions. Such particles are called fermions.

The Hartree–Fock approach is to recognize that all electrons are identical and to start with a determinantal wave function satisfying the Pauli principle.

$$\psi = k \begin{vmatrix} \phi_1(r_1, \sigma_1), \phi_1(r_2, \sigma_2) \dots \phi_1(r_N, \sigma_N) \\ \cdot \\ \cdot \\ \cdot \\ \phi_N(r_1, \sigma_1) \qquad \qquad \phi_N(r_N, \sigma_N) \end{vmatrix} \qquad (1.20)$$

(r, σ) denote the position and spin co-ordinates and k is a normalization constant ($k = 1/\sqrt{N!}$ if the ϕ's are orthonormal). It should be noted that if $\phi_i = \phi_j$, two rows are identical and the determinant vanishes. Only one electron may occupy a given spin-orbital. Similarly if $(r_i, \sigma_i) = (r_j, \sigma_j)$ two columns are identical and the determinant again vanishes. Two electrons with the same spin are never at the same position in space. The one-electron functions are again chosen to minimize the expectation value of the Hamiltonian (1.14) subject to the condition that each is normalized. It is necessary that the functions be linearly independent so that it is possible to form an orthogonal set from them (Adams, 1961).

The set of equations which the one-electron wave functions must satisfy can be written in the 'standard form'

$$\mathscr{H}_i\phi_i(r_1) = E_i\phi_i(r_1) \qquad (1.21)$$

where the one-electron Hamiltonians are given by

$$\mathscr{H}_i = -\frac{\hbar^2}{2m}\nabla_1{}^2 + V_L(r_1) + e^2 \sum_j^{\text{Parallel}} \int \frac{\phi_j{}^*(r_2)\phi_j(r_2)}{4\pi\epsilon_0 \,|\, r_1 - r_2 \,|}\mathrm{d}\tau_2$$

$$-e^2 \sum_j^{\substack{\text{Parallel}\\\text{spins}}} \int \frac{\phi_j{}^*(r_2)\phi_i{}^*(r_1)\phi_i(r_2)\phi_j(r_1)}{4\pi\epsilon_0 \,|\, r_1 - r_2 \,|\, \phi_i{}^*(r_1)\phi_i(r_1)}\mathrm{d}\tau_2 \qquad (1.22)$$

The first two terms correspond precisely to the first two terms in the Hartree Hamiltonian (1.19). The summation in the third term is over all the ground state electron wave functions including the ith and so represents the Coulomb potential energy of the electron in the average field of all the electrons including itself. The fourth term is summed only over the wave functions with spin parallel to the ith and is a new term brought about by the use of a determinantal wave function.

The equations (1.21) have two types of solutions. First of all there are the N one-electron wave functions which are occupied in the ground state of the system. Apart from these solutions there are an infinite number of solutions corresponding to unoccupied excited states. All the Hartree–Fock solutions have the advantage of being orthogonal to each other, a property the Hartree solutions do not possess.

The fourth exchange term in (1.22) must somehow compensate for the Coulomb self-interaction of an electron with itself which is physically not acceptable. If only the ith member of the summation in the exchange term is used, then the Hartree–Fock and the Hartree Hamiltonians are identical. The Hartree equations are not unreasonable for free atoms, for they represent an electron moving in the field of an ionized atom which is physically to be expected. However, if the atoms are assumed to form a crystal with a large enough lattice constant so that interatomic interactions are small, the Hartree equations instead of depicting electrons which, at any instant, are essentially moving in the field of an ionized atom, describe electrons which move in the field of a neutral atom.

This arises because the term omitted in the Hartree Hamiltonian for the self-interaction of an electron is now negligible as the wave functions are spread throughout the

crystal and not concentrated about an atom. Only an extremely small part of the charge density of a crystal wave function is associated with a particular atom site. Therefore it may be reasonable to use the Hartree equations for free atoms but not for crystals.

The Hartree–Fock equations correct for this fault of the simple Hartree solutions. An exchange charge density is defined by

$$\rho(r_2, r_1) = \sum_j^{\substack{\text{Parallel} \\ \text{spins}}} \frac{\phi_j^*(r_2)\phi_i(r_2)\phi_i^*(r_1)\phi_j(r_1)}{\phi_i^*(r_1)\phi_i(r_1)} \quad (1.23)$$

The Hartree–Fock equations (1.21) are ordinary Schrödinger equations of an electron moving in the field of the nuclei and of all the electrons including itself, diminished by the field due to the exchange charge (1.23).

If the ith state is occupied then

$$\int \rho(r_2, r_1)d\tau_2 = 1 \quad (1.24)$$

and so the ith electron moves in the Coulomb field of all the electrons with spin not parallel to it, but the charge of the electrons with parallel spins is diminished by one. This charge may be shown to be removed from the vicinity of the electron and constitutes the exchange hole. This means that the occupied solutions of the Hartree–Fock equations represent electrons moving in the field of the ion core and in the Coulomb field of $(N - 1)$ electrons where N is the total number of valence electrons.

If a state is not occupied in the ground state, it is clear that the exchange charge

$$\int \rho(r_2, r_1)d\tau_2 = 0$$

and so there is no exchange hole and the Coulomb potential arises from all the electrons. This is the type of potential an extra electron would be expected to experience if added to the N electrons already present and if its effect on the ground state

functions is ignored. Physically these results are sensible, and correct the results of the simple Hartree equations.

In practice the Hartree–Fock equations are solved in a self-consistent manner. An initial set of one-electron wave functions is taken and the Hamiltonian $\mathscr{H}_i$ obtained from equation (1.22). Then equations (1.21) are solved and a new set of wave functions obtained, and the whole process is repeated until the initial and final wave functions are in close enough agreement.

The Hartree–Fock equations have been applied to certain atoms but little application to solids has been made as yet due to the difficulties involved, although some greatly simplified methods have been used.

Koopmans (1933), has shown that the magnitude of the one-electron energies given by the equation (1.21), represent the ionization energies of the corresponding electrons when only one is excited. These energies are of great importance in the theory of electron bands.

It should be noted that the expectation value of the many-electron Hamiltonian (1.14) is less than the sum of the one-particle energies E_i as this sum counts each electron–electron interaction twice. (For further details of the one-electron approximation see Seitz, 1953.)

As an electron travels through the crystal, it repells other electrons and a 'Coulomb hole' is formed around it. There is correlation between the motion of the electrons. The use of an anti-symmetric wave function in the Hartree–Fock approach does take account of correlation between electrons of parallel spin, to a certain extent, but correlation between electrons of anti-parallel spin is ignored. Correlation reduces the total energy by keeping electrons apart and following the variational principle, the Hartree–Fock approach must be a better approximation than the Hartree method. The difference in the many-electron energy obtained by the Hartree and Hartree–Fock methods is called the exchange energy. This should not be given too much physical significance as it is just the difference between two mathematical approximations to the truth.

The total Hartree–Fock energy E_{HF} is defined by the expectation value of the full Hamiltonian for a crystal with fixed ions, obtained from a determinantal wave function. This is the expectation value of the Hamiltonian in (1.14) together with the inter-ionic repulsion terms

$$\tfrac{1}{2}\sum_i \sum_{i \neq j} W(\boldsymbol{R}_i - \boldsymbol{R}_j)$$

The ionic terms are added to avoid divergencies. For the ground state, the Hartree–Fock energy is an upper bound to the exact eigenvalue E. The energy error $(E - E_{HF})$ is called the 'correlation energy' and is a measure of the accuracy of the Hartree–Fock approach. The correlation energies for atoms are of the order of a few electron volts.

Even though the interaction between two electrons may be expected to be of the same magnitude as the interaction between an electron and an ion the same distance apart, the one-electron approximation is very useful as the following chapters will show. Bohm and Pines (1953) have indicated why the one-electron approximation gives such good results. They have shown that the screening effect of the mobile electrons limits the long-range Coulomb interaction between them, but this work is beyond the scope of this book.

The one-electron approximation is not sufficient to fully explain such phenomena as cohesive energy or ferromagnetism. The full set of solutions of the Hartree–Fock equations (1.21) form a complete set of one-electron functions. The totality of $N \times N$ determinantal wave functions, form a complete set of N-electron antisymmetric wave functions and so the exact solutions of the many-electron Schrödinger equation (1.14) may be expressed as a linear combination of these determinantal wave functions. This process is called 'configuration interaction'.

Problems for Chapter I

1. Write down the Schrödinger quantum operators representing the three Cartesian components of angular momentum.
Verify the commutation relation

$$\mathscr{L}_x\mathscr{L}_y - \mathscr{L}_y\mathscr{L}_x = i\hbar\mathscr{L}_z$$

2. An electron is constrained to remain inside a linear box of length $2a$ by walls of infinite potential. Inside the box the potential function is zero. Write down the Hamiltonian for the particle and find the normalized eigenfunctions for the time-independent Schrödinger equation.
Show that the allowed eigenvalues are given by

$$E_n = \frac{n^2\hbar^2}{32ma^2}$$

where n is restricted to integral values.

3. Prove that the eigenvalues of a Hermitian operator are real.

4. Prove that the eigenfunctions of a Hermitian operator, belonging to different eigenvalues, are orthogonal.

5. The Hamiltonian operator that describes the motion of an electron in a potential V is

$$\mathscr{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$$

Show that this Hamiltonian is Hermitian. The potential may be taken to be real and also to be a function of position only.

6. The classical Lagrangian for an electron of mass m and charge $-e$ in an electro-magnetic field is

$$L = \tfrac{1}{2}mV^2 + e\phi - e(V \cdot A)$$

V is the electron velocity and A and ϕ are the vector and scalar potentials of the field. Show that the component of momentum conjugate to x_i is

$$P_i = m\dot{x}_i - eA_i$$

Derive the classical Hamiltonian. Write down the corresponding quantum mechanical Hamiltonian.

$\left(\text{The component of momentum conjugate to } x_i \text{ may be defined by the Lagrange equation } p_i = \dfrac{\partial L}{\partial \dot{x}_i}.\right)$

7. One approximation to a metal is to consider the motion of a gas of N electrons of charge $-e$ in a volume Ω. To ensure the neutrality of the system a uniform background of positive charge is added, having a charge density equal to the average charge density of the electrons. In the Hartree approximation the one-electron functions satisfy the set of equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \int \frac{e}{4\pi\epsilon_0 \mid \boldsymbol{r}_1 - \boldsymbol{r}_2 \mid}\rho_+ \mathrm{d}\tau_2 \right. $$
$$\left. + e^2 \sum_j' \int \frac{\psi_j{}^*(\boldsymbol{r}_2)\psi_j(\boldsymbol{r}_2)}{4\pi\epsilon_0 \mid \boldsymbol{r}_1 - \boldsymbol{r}_2 \mid}\mathrm{d}\tau_2 \right]\psi_i(\boldsymbol{r}_1) = E_i\psi_i(\boldsymbol{r}_1)$$

The positive background charge density is $\rho_+ = Ne/\Omega$.

Show that the set of plane waves

$$\psi_k(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}}e^{i\boldsymbol{k}\boldsymbol{r}}$$

form a self-consistent solution of these equations if terms of the order of $e^2/(\Omega)^{\frac{1}{3}}$ are neglected.

(This result shows that the energy of the electron gas in this approximation is purely kinetic.)

8. In Problem 2, if the origin is taken at one end of the box, the electron wave functions are (ignoring spin)

$$\psi_n = \frac{1}{\sqrt{a}}\sin\left(\frac{n\pi}{2a}x\right) \qquad n = 1, 2, \ldots$$

Write down the spacial part of the determinantal wave function $\psi(x_1, x_2)$ describing two electrons, with identical spin, in the two lowest energy levels. If one electron is at the point $a/2$ in the linear box, the probability distribution of the other is $\psi^*\left(\frac{a}{2}, x_2\right)\psi\left(\frac{a}{2}, x_2\right)$. Confirm that this distribution is

$$\frac{1}{2a^2}\left[\sin\frac{\pi x_2}{2a} - \frac{1}{\sqrt{2}}\sin\frac{\pi x_2}{a}\right]^2$$

Sketch this function and explain how it illustrates the 'Fermi-Hole' concept. Compare this result with that obtained by the simple Hartree product wave function.

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2

Free-electron Model

§ 2.1 The Sommerfeld model

In the one-electron approximation, the wave equation to be solved is

$$-\frac{\hbar^2}{2m}\,\nabla^2\psi + V(r)\psi = E\psi \qquad (2.1)$$

The Hartree–Fock potential V takes account of the interactions of the electron with the ionic cores and with the averaged charge of the other electrons. Due to the positive point charges at each atom site, the potential must possess singularities and the
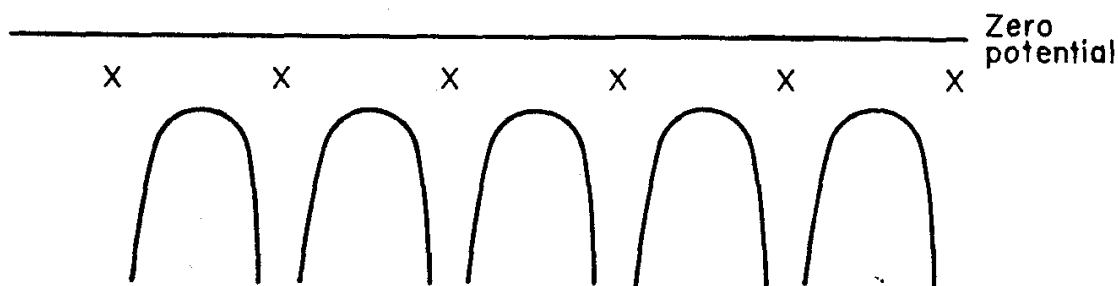

FIG. 2.1   Section through a line of atoms

potential plot along a section through a line of atoms is illustrated in Fig. 2.1.

In 1928 Sommerfeld suggested a model in which the potential is taken as a constant inside a metal so that the force acting on an electron is zero. Essentially, the metal is replaced by a box

containing a non-interacting gas of electrons; the free-electron gas. The electrons are not assumed altogether independent as they are taken to obey the Pauli principle. The free-electron gas does bear some relation to the state of the valence electrons in the alkali metals.

Consider a cube of side a with the origin of the co-ordinate system at a corner of the box. Inside the box the potential energy of an electron is negative (i.e. attractive) and equal to $-W$ and outside the box the potential energy is zero. The Schrödinger equation to be solved is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + (-W)\psi = E\psi \qquad 0 \leqslant \begin{matrix} x \\ y \\ z \end{matrix} \leqslant a$$

and

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = E\psi \qquad \begin{matrix} (2.2) \\ \text{otherwise} \end{matrix}$$

The wave functions and their derivatives must be continuous at the walls of the box and the bound state wave functions must also approach zero at infinity. As $W \sim 5$ eV for a metal then it can be shown that for a box of macroscopic dimensions ($a \sim 1$ cm) the wave functions are vanishingly small outside the box and consequently it is reasonable to use the simplified boundary conditions $\psi = 0$ at the box walls.

The equation to be solved is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + k^2\psi = 0 \qquad \text{inside the box} \quad (2.3)$$

where the electron kinetic energy

$$E_k = E - (-W)$$

$$= \frac{\hbar^2}{2m}k^2 \qquad (2.4)$$

This relation implies that k must be real. For the electron to be 'trapped' in the box the total energy must be negative and so $E_k < W$.

The partial differential equation (2.3) is solved by the method of separation of variables. By writing

$$\psi(x, y, z) = X(x)\,Y(y)Z(z) \tag{2.5}$$

equation (2.3) becomes

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{d^2y^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} + k^2 = 0 \tag{2.6}$$

The first term does not involve y or z, the second does not involve x or z and the third does not involve x or y. This means that

$$\frac{1}{X}\frac{d^2X}{dx^2} + k_x{}^2 = 0$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2} + k_y{}^2 = 0$$

$$\frac{1}{Z}\frac{d^2Z}{dz^2} + k_z{}^2 = 0 \tag{2.7}$$

where k_x, k_y, k_z are constants such that

$$k^2 = k_x{}^2 + k_y{}^2 + k_z{}^2 \tag{2.8}$$

Each of the equations (2.7) has a general solution of the form

$$X(x) = A \sin k_x x + B \cos k_x x \qquad k_x{}^2 > 0 \quad (a)$$
$$X(x) = Ax + B \qquad\qquad\qquad\quad k_x{}^2 = 0 \quad (b) \quad (2.9)$$
$$X(x) = A \sinh |\,k_x\,|\,x + B \cosh |\,kx\,|\,x \quad k_x{}^2 < 0 \quad (c)$$

where A, B are arbitrary constants.

The only solution which can satisfy the boundary conditions is (2.9(a)) and the wave function (2.5) is then composed of terms of the type

$$\frac{\sin}{\cos} k_x x \; \frac{\sin}{\cos} k_y y \; \frac{\sin}{\cos} k_z z \tag{2.10}$$

This wave function must vanish at all points on the cube surface and the only product satisfying this condition is

$$A \sin k_x x \,.\, \sin k_y y \,.\, \sin k_z z \tag{2.11}$$

with
$$k_x = l\frac{\pi}{a}, \; k_y = m\frac{\pi}{a}, \; k_z = n\frac{\pi}{a}$$

where l, m, n are integers. The electron kinetic energy is

$$E_k = \frac{h^2}{8ma^2}(l^2 + m^2 + n^2) \qquad (2.12)$$

It is clear from (2.11) that all the linearly independent solutions are obtained if l, m, n take positive values only. Observe that it is the application of the boundary conditions that quantizes the energy. The energy levels lie very close together ($\sim 10^{-15}$ eV apart) and for most purposes may be taken as continuous; the energy levels are said to be quasi-continuous. The total electron energy is

$$E = \frac{h^2}{8ma^2}(l^2 + m^2 + n^2) - W \qquad (2.13)$$

The number of electron states (neglecting spin) with kinetic energy less than some given energy E_k is easily obtained. It is the number of integral points within the positive octant of the sphere of radius r where

$$E_k = \frac{h^2}{8ma^2} \cdot r^2 \qquad (2.14)$$

For large values of r the number of the points is simply the volume of the octant

$$\frac{1}{8}\left(\frac{4}{3}\pi r^3\right)$$

So the number of electron states with energy less than E_k is

$$M(E_k) = \Omega \frac{\pi}{6}\left(\frac{8m}{h^2}\right)^{\frac{3}{2}} E_k^{\frac{3}{2}} \qquad (2.15)$$

where $\Omega = a^3$ is the volume of the box. If spin is considered the number of states is twice that given by equation (2.15). The number of states per unit energy range is called the density of states $N(E)$ and is related to $M(E)$ by

$$\int_0^{E_k} N(E)\mathrm{d}E = M(E_k) \qquad (2.16)$$

$$\therefore \qquad N(E_k) = \left(\frac{\mathrm{d}M}{\mathrm{d}E}\right)_{E_k} \qquad (2.17)$$

Hence

$$N(E_k) = \Omega \frac{\pi}{4}\left(\frac{8m}{h^2}\right)^{\frac{3}{2}} E_k^{\frac{1}{2}} \qquad (2.18)$$

Note that the number of states per unit energy per unit volume is independent of the dimensions of the box. Again, when spin is included the density of states is twice that given by (2.18). A more complete treatment shows that (2.18) is valid when non-cubic volumes are considered.

The solution of the wave equation given by (2.11) is a consequence of the particular boundary conditions imposed. Suppose that instead of a box in which the electrons are trapped, there is an infinity of such boxes stacked together and all identical. The appropriate boundary conditions are the cyclic or Born von Kármán conditions.

$$\psi(x + a, y, z) = \psi(x, y + a, z) = \psi(x, y, z + a)$$
$$= \psi(x, y, z) \qquad (2.19)$$

The normalized solutions of the wave equation (2.3) are now

$$\psi(x, y, z) = \frac{1}{\sqrt{\Omega}} e^{i(k_x x + k_y y + k_z z)} \qquad (2.20)$$

$$k_x = l\left(\frac{2\pi}{a}\right), \; k_y = m\left(\frac{2\pi}{a}\right), \; k_z = n\left(\frac{2\pi}{a}\right) \qquad (2.21)$$

where l, m, n are integers. Here the integers take all values, both positive and negative, as the corresponding solutions are linearly independent.

The electron kinetic energy is now

$$E_k = \frac{h^2}{2ma^2}(l^2 + m^2 + n^2) \qquad (2.22)$$

The formulae (2.15) and (2.18) still apply. This may at first seem surprising because of the factor-four difference in the right-hand sides of equations (2.12) and (2.22). However, when it is remembered that both positive and negative values of l, m, n are now to be considered, this result quickly follows.

(Note — when the radius of a sphere is halved the volume is decreased by a factor of eight.)

Suppose there are N 'non-interacting' electrons contained in the box at absolute zero temperature. If the electrons obeyed classical rules then all of them would be in the lowest level. But this is not the case as electrons must obey the Pauli principle which demands that no two electrons possess the same set of four quantum numbers. Three of these numbers are l, m, n of (2.22) (or (2.12)) and the fourth is spin. Each pair of states defined by l, m, n may be occupied by two electrons. At absolute zero the electrons occupy energy levels from zero to a maximum value E_m defined by

$$\frac{N}{2} = \Omega \frac{\pi}{6}\left(\frac{8m}{h^2}\right)^{\frac{3}{2}} E_m^{\frac{3}{2}}$$

i.e.

$$E_m = \left(\frac{h^2}{8m}\right)\left(\frac{3}{\pi}\right)^{\frac{2}{3}} n^{\frac{2}{3}} \qquad (2.23)$$

where n is the number of electrons per unit volume. The value of E_m which corresponds to the valence electron density in metals is of the order of a few electron volts. The average kinetic energy of the electrons is

$$\bar{E}_k = \int_0^{E_m} E_k N(E_k)\,\mathrm{d}E \Big/ \int_0^{E_m} N(E_k)\,\mathrm{d}E$$

$$= \frac{3}{5} E_m \qquad (2.24)$$

This result will be referred to again in the discussion of the cohesive energy of metals in Chapter 7.

At absolute zero there is a bounding energy below which all the electron states are filled and above which all states are unoccupied. As the temperature is increased some electrons are excited into higher states and the boundary between occupied and unoccupied states becomes blurred. In this case it is appropriate to talk about the probability of a state being filled and resort must be made to statistical mechanics.

§ 2.2 Fermi–Dirac statistics

The fundamental result of statistical mechanics is that the probability of the system being in an allowed state with energy E is proportional to $\exp(-E/kT)$ where k is the Boltzmann constant and T is the absolute temperature. This relation holds in quantum mechanics as well as in classical mechanics. However, it is only useful in quantum theory if the correct many-electron eigenstates are known. In the one-electron approximation the system is described in terms of the single electron eigenstates. The many-electron wave function must change sign under the interchange of any two electrons and this imposes a restriction on the allowed eigenstates of the complete system. Only two electrons can occupy the lowest pair of one-electron states (specified by l, m, n) and it is meaningless to talk about the probability of all the electrons (assumed more than two) occupying this lowest energy as that situation can not exist.

The Fermi–Dirac distribution law gives the probability that a single-electron state is occupied, remembering that the many-electron wave function must be antisymmetric with respect to interchange of electrons. Clearly the Fermi–Dirac law is not as fundamental as the Boltzmann law as it depends on a Hartree–Fock type of approximate wave function, but even so it is important and is derived below. (The reader is referred to Rushbrooke's book (1949) for a background to statistical mechanics and to Schrödinger's text (1946) for a more detailed study of quantum statistics.)

It is assumed that the electrons form a gas of 'independent', structureless particles. The electron interactions are either ignored completely or approximately taken into account in an average way by the Hartree–Fock method. The electrons are Fermi particles; they are identical and at most one can occupy a completely specified single-electron energy state. If the energy levels are extremely close together and almost form a continuum then it is possible to group the energy levels in bundles

and give each bundle a relevant average energy. This is certainly the case for the levels in a box of non-microscopic dimensions and is also true in crystals.

Suppose the ith bundle contains w_i states with an average energy E_i. It is assumed that w_i and the number of electrons n_i in the bundle are both large. Clearly $n_i < w_i$ as there is at most one electron in each state. The number of distinguishable ways of distributing the electrons among the states in the bundle is

$$\frac{w_i!}{n_i!(w_i - n_i)!} \qquad (2.25)$$

In deriving equation (2.25) it must be remembered that the electrons are identical and so distributions differing only by an interchange of electrons are equivalent. For a given set of distribution numbers n_i, the total number of distinguishable ways of arranging all the electrons among the states in all the bundles is

$$t = \prod_i \frac{w_i!}{n_i!(w_i - n_i)!} \qquad (2.26)$$

There are restrictions placed on (2.26). First, the sum of the distribution numbers must add up to the total number of electrons and second, the sum of the electron energies must equal the total energy E.

$$\sum_i n_i = N \quad (a)$$
$$\sum_i n_i E_i = E \quad (b) \qquad (2.27)$$

This latter condition requires further consideration. It has already been stated in Chapter 1 that the total energy of the system is not simply a sum over the one-electron Hartree–Fock energies. However, it can be shown that if the excited many-electron state is close to the ground state (i.e. only a few electrons are raised by a small amount) then the results obtained using the second of equations (2.27) are essentially correct. This is true for thermal excitations at ordinary temperatures (see Slater, 1956).

There are other sets of distribution numbers, apart from those in (2.26) which satisfy (2.27) and so give rise to other distinguishable arrangements of electrons. All such possible arrangements for a given total number of electrons and a given energy are taken to be equally probable. However, for sufficiently large N it can be shown that the observed averaged properties of the system are identical with those obtained from the most probable set of distribution numbers found by maximizing (2.26) subject to the conditions (2.27). In fact it is more convenient to maximize $\ln t$.

$$\ln t = \sum_i [\ln (w_i!) - \ln (n_i!) - \ln \{(w_i - n_i)!\}]$$

w_i and n_i are both large and if $(w_i - n_i)$ is also large then Stirling's approximation for the factorial may be used.

$$\ln (x!) \simeq x \ln x - x$$

A rigorous treatment would require some justification of these approximations, but it will suffice to note here that the final result obtained may be verified by more powerful methods.

$$\ln t = \sum_i [w_i \ln w_i - n_i \ln n_i - (w_i - n_i) \ln (w_i - n_i)]$$

The method of Lagrange multipliers is used to maximize $\ln t$ subject to the restrictions (2.27). Then

$$\frac{\partial}{\partial n_i} \left[\ln t + \alpha \left(\sum_i n_i - N\right) + \beta \left(\sum_i n_i E_i - E\right) \right] = 0 \text{ for all } i$$

where α, β are multipliers,

i.e. $\quad -\ln n_i - 1 + \ln (w_i - n_i) + 1 + \alpha + \beta E_i = 0$

and
$$n_i = \frac{w_i}{e^{-\alpha - \beta E_i} + 1} \tag{2.28}$$

α and β are of course determined by (2.28) together with the restrictive conditions (2.27). The entropy S is a function of the internal energy E, the number of electrons N and the volume Ω and is given by

$$S = k \ln t_{\max}.$$

where k is Boltzmann's constant. From the thermodynamic relations

$$\left(\frac{\partial S}{\partial E}\right)_{N,\Omega} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial N}\right)_{E,\Omega} = -\frac{\zeta}{T}$$

it is possible to identify β as $-1/kT$ and α as ζ/kT were ζ is the chemical potential per electron. In solid state theory ζ is generally referred to as the Fermi energy and denoted by E_F. The distribution function $f = n_i/w_i$ gives the probability that a given state is occupied and

$$f(E_i) = \frac{1}{e^{[E_i - E_F]/kT} + 1} \qquad (2.29)$$

This is the Fermi–Dirac distribution law. At $T = 0$, $f = 1$ for $E_i < E_F$ and $f = 0$ for $E_i > E_F$. All states with energies less than E_F are filled whereas those with energies greater than
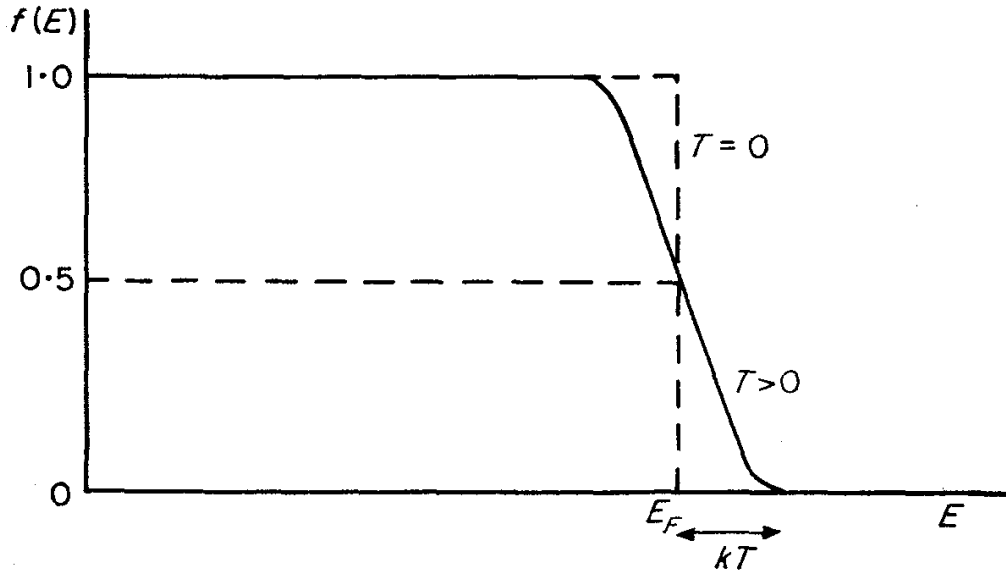

FIG. 2.2 Fermi distribution

E_F are empty. As the temperature is increased from absolute zero the distribution function departs from this step character. Some electrons in the states immediately below E_F are excited into levels just above. The only region where f is appreciably different from one or zero is in the neighbourhood of E_F over a

range of energies of the order of kT. The Fermi energy is itself a function of temperature but when $kT << E_F(T)$ it can be shown that it changes only slightly from the value at $T = 0$. At all temperatures f has the value $\frac{1}{2}$ when $E_t = E_F$. For high electron energies where $E_t >> E_F$, f behaves like the high energy tail of the classical Boltzmann distribution.

The criterion for quantum statistics to be necessary is that the Pauli principle be important. This occurs when there are 'too many' electrons for the available energy levels. If classical statistics are obeyed then almost all the electrons will have energies up to $\sim kT$ and at room temperature this is $\sim \frac{1}{40}$ eV. Silver is a 'typical' monovalent metal where one electron per atom is denoted to a sea of loosely bound conduction electrons. In one mole of silver, the volume of which is ~ 10 cc, the number of electron states with energies less than $\frac{1}{40}$ eV is $\sim 10^{20}$ (see 2.15). But one mole of silver contains 10^{23} conduction electrons. There are far more electrons than states available and certainly quantum statistics must be used. This is the case for metals where to accommodate all electrons, states up to about 5 eV are filled. More formally, quantum statistics is necessary when $kT << E_F$ and then the electron gas is said to be degenerate. A degeneracy temperature may be defined by $kT_0 = E_F(0)$ and the condition for degeneracy is $T << T_0$. For metals $T_0 \sim 10^{4}°K$.

§ 2.3 Variation of the Fermi energy with temperature

The Fermi energy is not constant but decreases slowly as the temperature rises. The relation is obtained below.

An important property of the Fermi–Dirac function is that its derivative differs from zero only in the neighbourhood of the Fermi energy.

With this in mind consider the integral

$$I = \int_0^\infty f(E)\frac{\mathrm{d}}{\mathrm{d}E}G(E)\mathrm{d}E \qquad (2.30)$$

where $f(E)$ is the Fermi function and $G(E)$ is any function such that $G \longrightarrow 0$ as $E \longrightarrow 0$. Integrating by parts

$$I = \left[f(E)G(E) \right]_0^\infty - \int_0^\infty G(E)\frac{\mathrm{d}f}{\mathrm{d}E}\mathrm{d}E \qquad (2.31)$$

The properties of $f(E)$ and $G(E)$ make the first term on the r.h.s. vanish at the upper and lower limits respectively. If $G(E)$
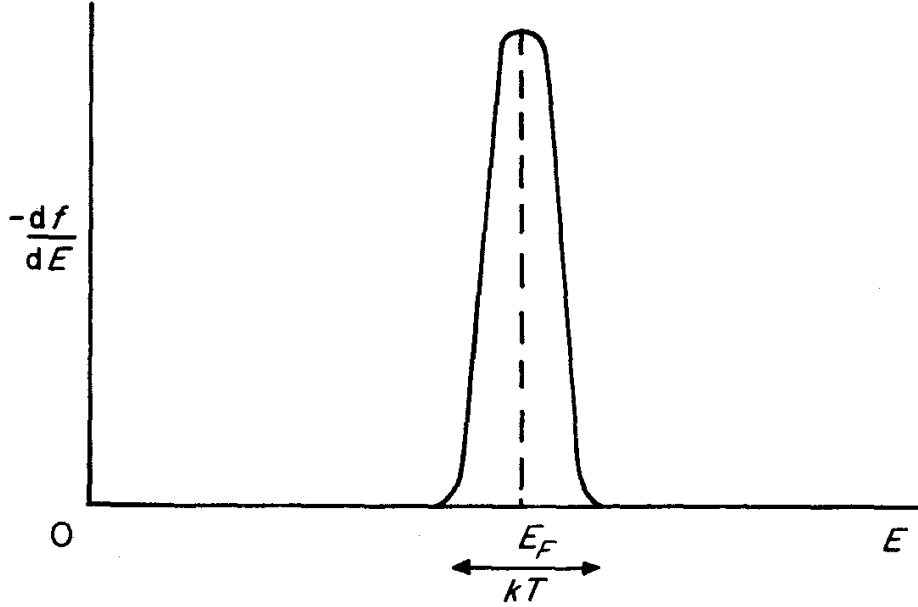

FIG. 2.3   Derivative of the Fermi function

does not possess a singularity at E_F it may be expanded by Taylor series and within its radius of convergence.

$$G(E) = G(E_F) + (E - E_F)G'(E_F)$$
$$+ \tfrac{1}{2}(E - E_F)^2 G''(E_F) + \ldots \qquad (2.32)$$

Then

$$I = -\int_0^\infty [G(E_F) + (E - E_F)G'(E_F)$$
$$+ \tfrac{1}{2}(E - E_F)^2 G''(E_F) + \ldots]f'(E)\mathrm{d}E \qquad (2.33)$$

Assuming term by term integration

$$I = -L_0 G(E_F) - L_1 G'(E_F) - L_2 G''(E_F) - \ldots \qquad (2.34)$$

with
$$L_0 = \int_0^\infty f'(E)\,\mathrm{d}E = \Big[f'(E)\Big]_0^\infty = -1$$

$$L_1 = \int_0^\infty (E - E_F)f'(E)\,\mathrm{d}E = 0$$

$$L_2 = \tfrac{1}{2}\int_0^\infty (E - E_F)^2 f'(E)\,\mathrm{d}E \neq 0 \qquad (2.35)$$

To calculate L_2 it is useful to substitute $x = (E - E_F)/kT$ and then

$$L_2 = -\frac{(kT)^2}{2}\int_{-E/kT}^\infty \frac{x^2 e^x}{(1 + e^x)^2}\,\mathrm{d}x$$

In metals $kT << E_F$ and the lower limit may be replaced by $-\infty$ and so (see any standard table of definite integrals)

$$L_2 \simeq -\frac{\pi^2}{6}(kT)^2 \qquad (2.36)$$

The integral I is

$$I = G(E_F) + \frac{\pi^2}{6}(kT)^2 G''(E_F) + \ldots \qquad (2.37)$$

From this very useful result it is possible to show how the Fermi energy varies with temperature. To do this put $G(E)$ equal to the total number of electron states (including spin) with energy less than E.

$$G(E) = 2\int_0^E N(E)\,\mathrm{d}E \quad \text{so that} \quad G'(E) = 2N(E)$$

With this choice I represents the total number of electrons N.

$$N = 2\int_0^{E_F} N(E)\,\mathrm{d}E + \frac{\pi^2}{3}(kT)^2 N'(E_F) + \ldots \qquad (2.38)$$

N is also given by

$$N = 2\int_0^{E_F(0)} N(E)\,\mathrm{d}E \qquad (2.39)$$

where $E_F(0)$ is the Fermi level at absolute zero. From these last two equations

$$\int_{E_F(0)}^{E_F} N(E)\,\mathrm{d}E \simeq -\frac{\pi^2}{6}(kT)^2 N'(E_F)$$

As $E_F - E_F(0)$ is small then

$$[E_F - E_F(0)]N(E_F(0)) \simeq -\frac{\pi^2}{6}(kT)^2 N'(E_F(0))$$

i.e.
$$E_F \simeq E_F(0) - \frac{\pi^2}{6}(kT)^2 \left(\frac{d}{dE}\ln N\right)_{E_F(0)} \qquad (2.40)$$

For free electrons N is given by (2.18) and $E_F(0)$ is the maximum electron energy (2.23).

$$E_F \simeq E_m\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_m}\right)^2\right] \qquad (2.41)$$

The Fermi energy falls as the temperature increases but the change is only of second order in kT/E_F. At room temperature $kT/E_F \sim 10^{-3}$ for metals.

§ 2.4 Electron specific heat

If electrons were classical particles then an energy of $kT/2$ would be associated with each degree of freedom and the internal energy of a gas of N non-interacting electrons would be

$$U = \tfrac{3}{2} NkT$$

The heat capacity is defined by

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

and so $C_v = 3Nk/2$. This constant value is not observed and experiment shows that C_v decreases linearly to zero as $T \longrightarrow 0$. This latter effect is due to the fact that electrons are Fermi particles.

The total kinetic energy (the energy zero is chosen here to be the base of the Fermi distribution) of the electrons in the volume Ω is

$$U = 2\int_0^\infty Ef(E)N(E)dE \qquad (2.42)$$

The factor two arises as each state may contain two electrons. Define

$$G(E) = 2\int_0^E EN(E)\mathrm{d}E$$

and from (2.37) at sufficiently low temperatures

$$U \simeq 2\int_0^{E_F} EN(E)\mathrm{d}E + \frac{\pi^2}{3}(kT)^2\frac{\mathrm{d}}{\mathrm{d}E}(EN(E))_{E_F} \quad (2.43)$$

The first term on the r.h.s. may be expanded by Taylor series.

$$2\int_0^{E_F} EN(E)\mathrm{d}E \simeq 2\int_0^{E_F(0)} EN(E)\mathrm{d}E$$
$$+ 2[E_F - E_F(0)]E_F(0)N(E_F(0))$$

The first term on the right is the kinetic energy U_0 of the electrons at absolute zero and the second is (2.40)

$$-\frac{\pi^2}{3}(kT)^2E_F(0)N'(E_F(0))$$

The total kinetic energy at temperature T is then

$$U = U_0 + \frac{\pi^2}{3}(kT)^2N(E_F(0)) \qquad (2.44)$$

and the heat capacity of the electrons is

$$C_v = \tfrac{2}{3}\pi^2 k^2 N(E_F(0))\,T \qquad (2.45)$$

This expression is a good approximation for most metals at all temperatures for which they are in the solid state. This linear contribution of the electrons to the heat capacity is only observed at very low temperatures since at higher temperatures it is swamped by the contribution from the lattice vibrations which tend to zero as T^3. For free electrons $N(E)$ is given by (2.18) and this result together with (2.23) may be used to express C_v in terms of the total number of electrons.

$$C_v = \tfrac{3}{2}Nk\left(\frac{\pi^2 k}{3E_m}\right)T \qquad (2.46)$$

This model can be used to represent a monovalent metal if N is made equal to the number of atoms in the volume. (For one mole of the metal $Nk = R$, the gas constant). Equation (2.46) is in quite good agreement with experiment. If there is some doubt about the number of free electrons per atom measurements of C_v can be used to give information about the density of states at the Fermi level.

Comparison of (2.46) and the classical value suggest that as $kT << E_m$ the number of electrons that may be considered free is much less than the total number of electrons. This result is a direct consequence of the Fermi–Dirac statistics. Only those electrons near the Fermi level are 'free' as they alone are able to be excited into higher energy states without an improbable energy jump.

§2.5 Weak spin paramagnetism

The magnetic properties of an atom are due to the orbital motion of the electrons and to their spins. The nuclear magnetic moment is negligible in comparison. The magnetic materials that occur in nature may be divided into four basic types:

(a) ferromagnetic
(b) antiferromagnetic
(c) diamagnetic ⎫
(d) paramagnetic ⎭ include most metals

These will now be discussed very briefly.

Below a certain temperature (Curie temperature) ferromagnetic substances are spontaneously magnetized and this is caused by an ordered coupling of parallel atomic magnetic moments. Examples are iron and nickel. In antiferromagnetic materials there is also an ordered coupling of atomic magnetic moments but arranged in antiparallel pairs so that there is no permanent macroscopic magnetic moment. There is also an intermediate class, the ferrimagnetic materials where the

atomic moments are antiparallel but not equal, so that there is a permanent magnetic moment.

For both diamagnetic and paramagnetic substances the magnetic moment per unit volume M is proportional to the applied magnetic field H.

$$M = \chi H$$

The constant of proportionality χ is called the susceptibility per unit volume.

If χ is negative, the material is diamagnetic and the magnetization is in the opposite direction to the field. This is an example of Lenz's law and may be explained by the induced Larmor procession of both the free and ionic electrons. Diamagnetism may be expected to occur in saturated materials whose constituents do not possess permanent magnetic moments. Induced magnetization of this type is generally very small ($| \chi | \sim 10^{-5}$) and temperature independent.

If χ is positive, the induced magnetization is parallel to the field and the substance is said to be paramagnetic. A few substances are strongly paramagnetic ($\chi \sim 10^{-3}$) and this is due to the orientation of the permanent magnetic moments of the constituents along the field. This can only happen if the dipoles can orient themselves freely in an applied field. Thermal motion acts to oppose this effect and it can be shown that the susceptibility obeys the Langevin formula and is inversely proportional to the absolute temperature

$$\chi = N m_c{}^2 \mu_0 / 3kT \qquad (2.47)$$

N is the number of magnetic cores per unit volume and m_c the magnetic moment of the core. Crystals containing rare earth ions exhibit this type of magnetization. Their paramagnetism is due to the magnetic moments of the inner incomplete shell.

Many metals have a weak temperature independent paramagnetic susceptibility of the order of 10^{-6}. This is due to the spin of the conduction electrons. The Langevin formula (2.47) predicts that the susceptibility be temperature dependent and much larger than that observed at room temperature. The

reason why the Langevin theory fails is that the electrons can not orient themselves freely in an applied field but must obey Fermi–Dirac statistics. Pauli (1927) gave the correct theory.

Paramagnetism of free electrons

The electron has a spin magnetic moment m_s equal to one Bohr magneton.

$$m_s = \frac{e\hbar}{2m} \qquad (2.48)$$

In an external magnetic field H, the energy of a static electron can have one of two possible values.

$$\pm m_s B \qquad B = \mu H \qquad (2.49)$$
$$(\mu \text{ is the permeability})$$

The minus and plus sign apply when the electron spin is parallel and antiparallel to the field respectively. If there was nothing to prevent it all the antiparallel electrons would orientate themselves parallel to the field, each transferring an energy $2m_s B$ to the lattice vibrations. In a free-electron gas this is not possible for most electrons as the states with parallel spins are already filled. However, at non-zero temperatures, there is always a small number of electrons in excited states and so electrons near the Fermi surface may be able to change their spin direction.

If it is assumed that the spacial movement of the electrons is unaffected by the magnetic field then the two degenerate electron states with initial energy E split into states with energies

$$E \mp m_s B \qquad (2.50)$$

The number of electron states per unit volume with spins parallel to the field in the energy range E to $E + dE$ is

$$\frac{1}{\Omega} N(E + m_s B) dE \qquad (2.51)$$

Ω is the volume in which the electrons are contained and $N(E)$ denotes the density of states (neglecting spin (2.18)) in the

absence of the field. The number of states with spin anti-parallel to the field is

$$\frac{1}{\Omega} N(E - m_s B) \mathrm{d}E \qquad (2.52)$$

The magnetic moment per unit volume is then

$$M = \frac{m_s}{\Omega} \int_0^\infty [N(E + m_s B) - N(E - m_s B)] f(E) \mathrm{d}E \quad (2.53)$$

where $f(E)$ is the Fermi–Dirac function (2.29).

In practice the magnetic field is very weak and

$$N(E + m_s B) - N(E - m_s B) = \frac{\mathrm{d}N}{\mathrm{d}E} 2 m_s B \quad (2.54)$$

The susceptibility per unit volume is then

$$\chi = 2 \frac{m_s^2}{\Omega} \mu_0 \int_0^\infty f(E) \frac{\mathrm{d}N}{\mathrm{d}E} \mathrm{d}E \text{ as } \mu \sim \mu_0 \qquad (2.55)$$

From (2.37), for sufficiently low temperatures

$$\chi = \frac{2 m_s^2}{\Omega} N(E_F) \mu_0 + \mu_0 \frac{m_s^2}{\Omega} \frac{\pi^2}{3} (kT)^2 \left[\frac{\mathrm{d}^2 N}{\mathrm{d}E^2} \right]_{E_F} \quad (2.56)$$

For all normal temperatures the first term is dominant and for free electrons N is given by (2.18).

$$\chi = \frac{3}{2} \frac{m_s^2 n}{E_m} \mu_0 \qquad (2.57)$$

where n is the number of electrons per unit volume. If $n \sim 10^{23}$ cm^{-3} and $E_m \sim 5$ eV then $\chi \sim 10^{-6}$ in quite good agreement with the alkalis. It should be noted that the diamagnetic effects of the magnetic field on the electron motion have been ignored. Landau (1930) has shown that for free electrons this susceptibility is equal to $-\frac{1}{3}$ of the paramagnetic susceptibility obtained above. The total susceptibility of the free electron gas is

$$\chi = \frac{m_s^2 n}{E_m} \mu_0 \qquad (2.58)$$

Problems for Chapter 2

1. The potential in a one-dimensional problem is defined by

$$V = -W \quad |x| \leqslant a, \quad V = 0 \quad |x| > a, \quad W > 0$$

Solve the time-independent Schrödinger equation using the correct boundary conditions

(a) $\psi \longrightarrow 0$ as $|x| \longrightarrow \infty$. (Bound state.)

(b) ψ and $\dfrac{d\psi}{dx}$ are continuous at $|x| = a$.

Show that if $\sqrt{\dfrac{2m\,|E|}{\hbar^2}} \cdot a >> |$ then the simplified boundary conditions, $\psi = 0$ at $|x| = a$ may be used. Sensible values for a metal are $|E| \sim 5$ eV and $a \sim 1$ cm. Confirm that in this case the simplified boundary conditions are valid.

2. The potential in a three-dimensional problem is defined by

$$V = -W \quad r \leqslant a, \quad V = 0 \quad r > a, \quad W > 0$$

(r is a spherical polar co-ordinate).

The eigenfunctions satisfy the conditions

(a) ψ is finite at $r = 0$.

(b) ψ and $\dfrac{d\psi}{dr}$ are continuous at $r = a$.

(c) $\psi \longrightarrow 0$ as $r \longrightarrow \infty$. (Bound state.)

Show that the spherically symmetric bound solutions ($E < 0$) are of the form

$$\psi = \frac{A}{r}e^{-\alpha r} \quad r > a \qquad\qquad \alpha = \sqrt{\frac{-2mE}{\hbar^2}}$$

$$\psi = \frac{B}{r}\sin \beta r \quad r \leqslant a \qquad\qquad \beta = \sqrt{\frac{2m}{\hbar^2}(W + E)}$$

Verify that a necessary condition for a non-trivial solution is

$$\alpha a = -\beta a \cot (\beta a)$$

α and β must also satisfy

$$(\alpha a)^2 + (\beta a)^2 = \frac{2m}{\hbar^2} W a^2$$

Illustrate these conditions graphically.

Explain why bound solutions exist only if

$$\sqrt{\frac{2mW}{\hbar^2}}\, a > \frac{\pi}{2}$$

$$\left[\text{The spherically symmetric Laplacian is } \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right). \right]$$

3. An electron is confined in a cylinder of radius a and length l. The potential inside the cylinder is $-W$ ($W > 0$) and is zero outside. If the co-ordinate axes are chosen so that the z-axis coincides with the cylinder axis and the origin is at the centre of the lower plane end then Schrödinger's equation is, in cylindrical polars (ρ, ϕ, z)

$$-\frac{\hbar^2}{2m}\left[\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho\frac{\partial}{\partial \rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2}\right]\psi - [W + E]\psi = 0$$

$$\rho < a \qquad 0 < z < l \qquad 0 < \phi < 2\pi$$

If $|E|$ is sufficiently large the boundary conditions reduce to $\psi = 0$ on the cylinder boundary. By the method of separation of variables show that the solutions finite and single-valued within the cylinder are of the form

$$\psi = A \sin \frac{n\pi}{l}z \cdot J_r(\alpha\rho) \frac{\cos r\phi}{\sin r\phi}$$

where n is a positive integer, r is a positive integer or zero and $J_r(\alpha a) = 0$. Verify that the corresponding eigenvalues are

$$E = \frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{l^2} + \alpha^2\right) - W$$

$$\left(\text{The Bessel function } J_r(x) \text{ is a solution of}\right.$$

$$\left.\frac{d^2y}{dx^2} + \frac{1}{x}\frac{dy}{dx} + \left(1 - \frac{r^2}{x^2}\right)y = 0\right)$$

4. The entropy of a system is a function of the total energy E, the number of constituents N and the volume Ω. Assuming that $S = k \ln t_{\max}$. show that for the free-electron gas

$$\frac{S}{k} = -N\alpha - E\beta + \sum_i w_i \ln (1 + e^{\alpha}e^{\beta E_i})$$

From the thermodynamic relations

$$\left(\frac{\partial S}{\partial E}\right)_{\Omega, N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial N}\right)_{E, \Omega} = -\frac{\zeta}{T}$$

and the restrictive conditions (2.27) show that

$$\beta = -\frac{1}{kT} \qquad \alpha = \frac{\zeta}{kT}$$

(α, β must be regarded as functions of E, N, Ω.)

5. It has been stated in the text (2.2) that the probability of a system being in a state with energy E is proportional to $\exp(-E/kT)$. Illustrate how this is consistent with the Fermi–Dirac distribution (2.29). To do this consider two energy states of the entire system which differ only by the excitation of a single electron. Initially the ith one-electron state is occupied and the jth state empty. In the final configuration the jth state is filled and the ith state empty, all the other electrons remaining unchanged. From the Fermi–Dirac law show that the ratio of the probability of the final state to that of the initial state is

$$\exp[(E_i - E_j)/kT]$$

(Note: the probability of the ith state not being filled is $[1 - f(E_i)]$.)

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3

The Importance of Crystal Symmetry

§ 3.1 The Bravais lattice

The fundamental property intrinsic to crystalline solids is their degree of order, whereas gases and liquids are in a state of disorder. The most important manifestation of this order is translational symmetry. A crystal has a periodic structure. There are, of course, deviations in real crystals, both at the surface, where the periodicity condition obviously breaks down, and also due to dislocations, impurities, and other imperfections in the interior. In most cases these can be considered as perturbations of an ideal crystal.

Solids possess symmetry properties apart from translational symmetry. These are the reflection planes and rotation axes which help to determine the external appearance of a crystal. From the crystallographic viewpoint, the rotation-reflection symmetry elements are most useful in the classification of crystals, but to the solid-state theorist the translational symmetry property is of greater consequence.

As crystals possess translational symmetry, it must be possible to define a minimum periodic displacement in any direction. Any two points separated by such a displacement must be equivalent in every respect. For a set of identical points placed at equal intervals along a straight line, the distance between any two consecutive points is the minimum repeating distance. In the case of a multi-dimensional periodic array of points, the

minimum periodic displacement is very long for most directions. However, for a two-dimensional array, it is possible to define two basis vectors, a_1 and a_2, so that all the equivalent points are given by

$$R_n = n_1 a_1 + n_2 a_2 \qquad (3.1)$$

where n_1, n_2 are integers. Such an array is called a Bravais net. Similarly for a three-dimensional array of points, it is possible to choose three basis vectors, a_1, a_2, a_3 so that all the equivalent points in the Bravais lattice are given by

$$R_n = n_1 a_1 + n_2 a_2 + n_3 a_3 \qquad (3.2)$$

where n_1, n_2 and n_3 are integers.
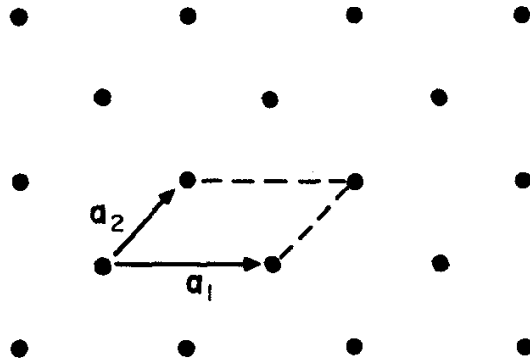
FIG. 3.1   Rhombic Bravais net

The basis vectors for a lattice are not unique, but they must satisfy the requirement that all the equivalent points in the lattice are given by equation (3.2) with a suitable choice for the integers n_i. In addition, all integral choices of n_i must represent a lattice point. A suitable set of basis vectors may be obtained as follows:

a_1 is taken as the shortest possible periodic length in the lattice;

a_2 is the next shortest length not parallel to a_1; and

a_3 is the next shortest length not co-planor with a_1 and a_2.

The three basis vectors define a parallelepiped which is called a primitive cell. The primitive cell has a volume given by

the triple product $a_1 \cdot (a_2 \wedge a_3)$ and is the smallest unit which will build up the lattice by periodic repetition. Different choices for the basis vectors yield different primitive cells but they all have the same volume. This can be understood if it is observed that one lattice point is associated with each primitive cell, and so for a given density of lattice points the primitive cell volume is fixed.

A Bravais lattice has other symmetry properties apart from translational symmetry. A centre of inversion is a point such that the lattice is invariant under the operator $r \longrightarrow -r$ where r
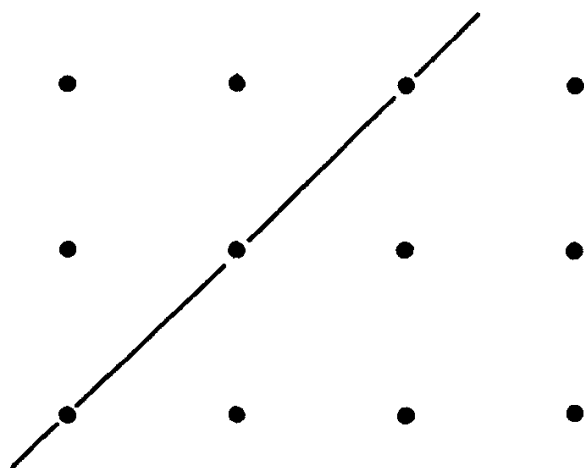
FIG. 3.2   Square Bravais net with line of symmetry

is the vector displacement of any point in the lattice referred to the inversion centre. A plane of symmetry is a plane in the lattice such that the lattice points on one side of the plane are mirror images of those on the other.

An axis of rotational symmetry is an axis such that the lattice takes up an identical position on rotation through a suitable angle about it. The angle of the rotation must be of the form $2\pi/n$ where n is an integer and such an axis is called an n-fold axis. A Bravais lattice may also possess a rotation-inversion axis if it is brought into self-coincidence by a rotation followed by an inversion. A two-fold inversion axis is equivalent to a mirror plane perpendicular to the axis (Fig. 3.3).

An infinite periodic array of points is invariant under a translational of the form (3.2). This condition leads to certain theorems regarding the presence of rotation-reflection symmetry elements. For example, it can be shown that a Bravais lattice has inversion symmetry about each lattice point and also about the midpoints of the lines joining two lattice points.
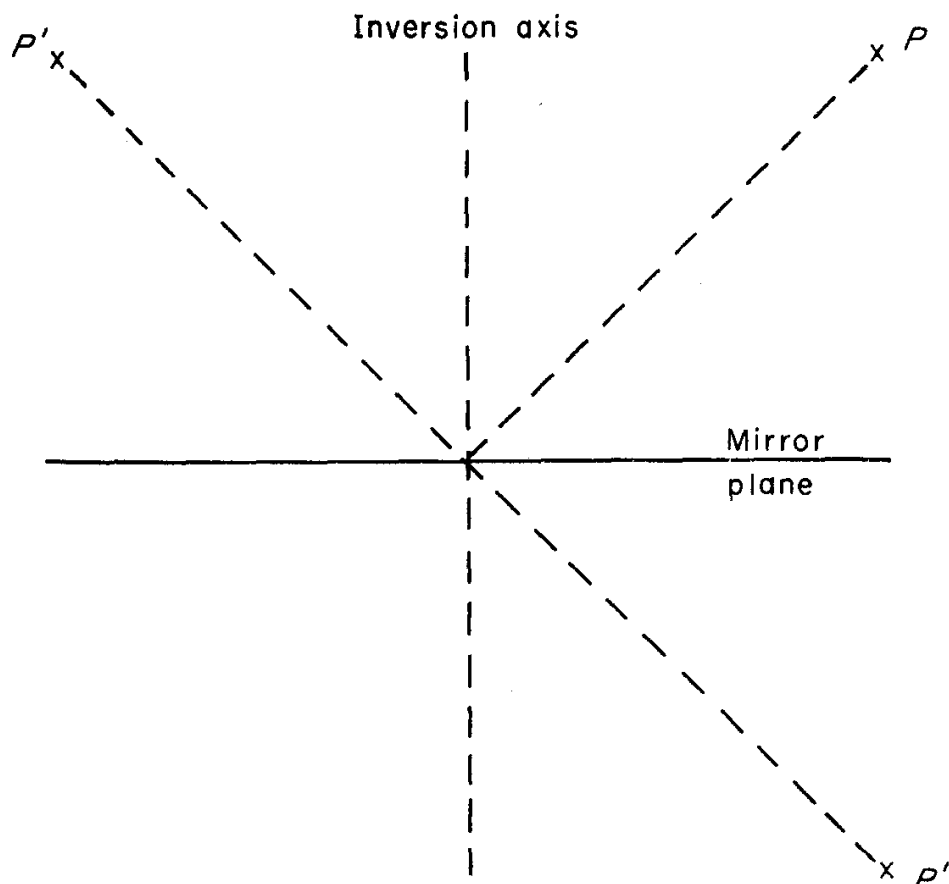

FIG. 3.3   A two-fold inversion axis is equivalent to a perpendicular mirror plane

However, actual crystal structures may lack this symmetry due to the distribution of atoms associated with each lattice point. An important result is that a Bravais lattice can only have an axis of two-, three-, four- or six-fold symmetry. There are no five-fold axes of symmetry in lattices although this restriction does not apply to physical systems lacking translational symmetry such as molecules.

There are fourteen possible ways of positioning structureless points in space such that all points have identical surroundings. These are the fourteen Bravais lattices. Each of these fourteen

Cubic unit cell

Rhombohedral primitive cell
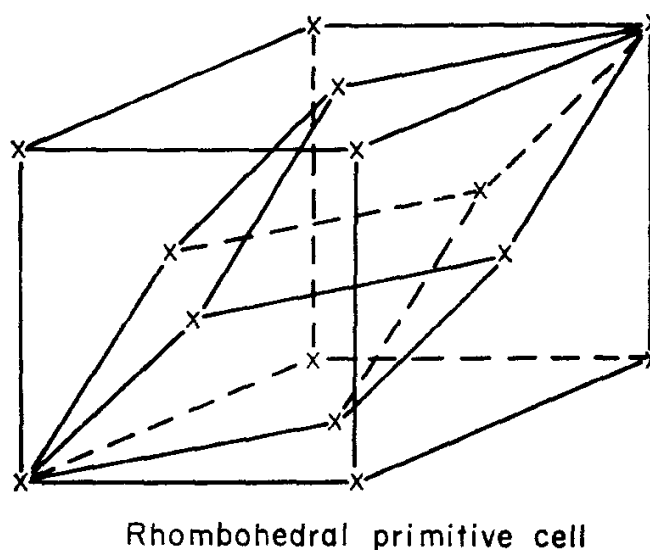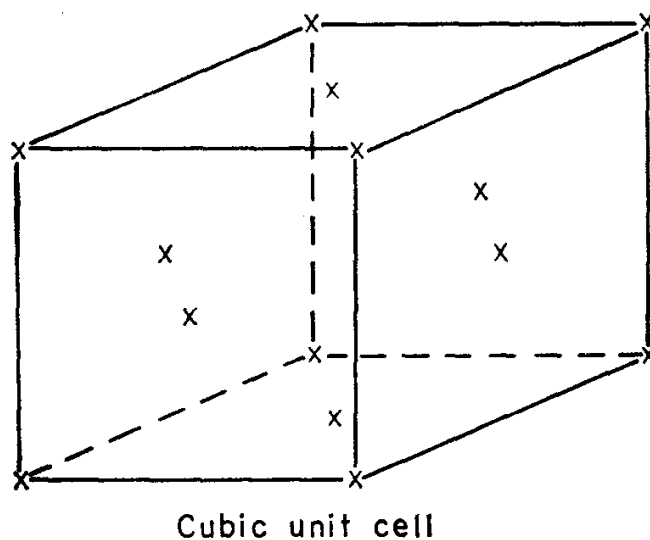
FIG. 3.4   Face-centred cubic lattice

Bravais lattices belongs to one of seven crystal systems which are characterized by the groups of symmetry elements associated with the lattice points. There are three Bravais lattices belonging to the cubic system, each of which has the same collection of

symmetry elements at the lattice points. Table (3.1) lists the different lattices and the corresponding crystal systems.

The primitive cell has been defined as the smallest repeating volume in the lattice, and has only one lattice point associated with it. This parallelepiped often disguises the lattice symmetry

TABLE 3.1

Crystal system	Bravais lattice
Triclinic	Simple
Monoclinic	Simple
	Base-centred
Orthorhombic	Simple
	Base-centred
	Face-centred
	Body-centred
Tetragonal	Simple
	Body-centred
Hexagonal	Simple
Rhombohedral	Simple
Cubic	Simple
	Face-centred
	Body-centred

and it is sometimes useful to introduce a larger cell which illustrates the symmetry more clearly. Such a cell will be associated with more than one lattice point and is called a unit cell. Figure 3.4 shows a primitive cell for the face-centred cubic lattice and also the corresponding cubic unit cell four-times the size, containing four lattice points.

§ 3.2 Symmetry operators

When a body possesses symmetry, it must be possible to bring it into self-coincidence by some symmetry operations, such as a rotation or reflection. A physical rotation of a body through an
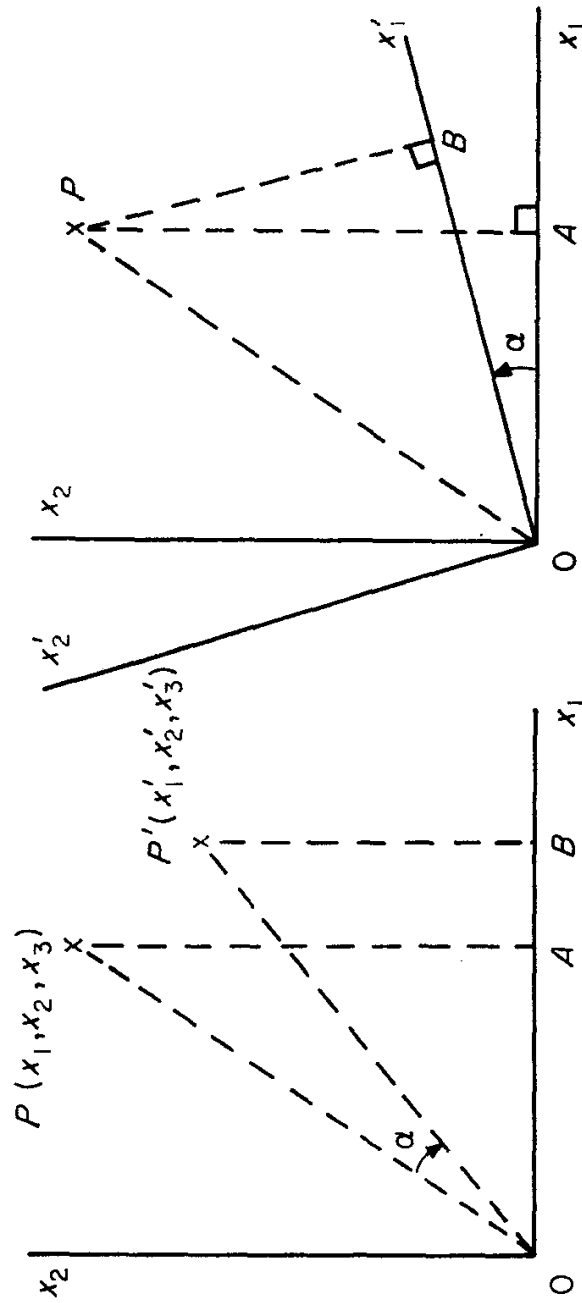
Fig. 3.5   (a) Rotation of P to P' in clockwise direction

$$OA = OB\cos\alpha - BP'\sin\alpha$$
$$AP = OB\sin\alpha + BP'\cos\alpha$$

(b) Rotation of axes in anti-clockwise direction

$$OA = OB\cos\alpha - BP\sin\alpha$$
$$AP = OB\sin\alpha + BP\cos\alpha$$

angle α in the clockwise direction about an axis, say the x_3-axis, is equivalent to a rotation of the axes system through the same angle in the anti-clockwise direction, in the sense that the relation between the new and old co-ordinates of any point in the body is the same in both cases (Fig. 3.5).

In each case

$$x_1 = x_1' \cos \alpha - x_2' \sin \alpha$$
$$x_2 = x_1' \sin \alpha + x_2' \cos \alpha \qquad (3.3)$$
$$x_3 = x_3'$$

x_1, x_2, x_3 and x_1', x_2', x_3' represent the old and new co-ordinates respectively.

In thinking about the symmetry properties of molecules and crystals, it is very useful to interpret the symmetry operations 'actively' in the sense of actual rotations of the physical system, but mathematically it is far more convenient to use the 'passive' viewpoint of axes rotation. In crystalline solids, the most general symmetry operation is a rotation, reflection or inversion about the origin, followed by a translation. Following the passive viewpoint, the new co-ordinates x_1', x_2', x_3' of a point, are given in terms of the old co-ordinates x_1, x_2, x_3 by a linear relation of the form

$$x_1' = \alpha_{11}x_1 + \alpha_{12}x_2 + \alpha_{13}x_3 + t_1$$
$$x_2' = \alpha_{21}x_1 + \alpha_{22}x_2 + \alpha_{23}x_3 + t_2 \qquad (3.4)$$
$$x_3' = \alpha_{31}x_1 + \alpha_{32}x_2 + \alpha_{33}x_3 + t_3$$

The matrix (α_{ij}) represents the rotational part of the operator and t_i represents the ith component of the translation. In matrix formulation

$$\begin{pmatrix} x_1' \\ x_2' \\ x_3' \end{pmatrix} = \begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} + \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix} \qquad (3.5)$$

or $$\boldsymbol{x}' = \alpha\boldsymbol{x} + \boldsymbol{t} \qquad (3.6)$$

The notations (3.4), (3.5) and (3.6) will be used as required.

For a pure rotation or reflection about the origin, the translation components are zero. Then the distance of a point from the origin remains constant and

$$r^2 = x_1{}^2 + x_2{}^2 + x_3{}^2 = x_1{}'^2 + x_2{}'^2 + x_3{}'^2 \quad (3.7)$$

The matrix (α_{ij}) is an orthogonal matrix and the determinant

$$|\alpha| = \pm 1$$

A convenient notation for representing transformations of the type (3.5) is that introduced by Seitz. The symbol $\{\alpha \mid t\}$ denotes a rotation (inversion or reflection), about the origin, followed by a translation t. $\{\epsilon \mid 0\}$ denotes the identity operator.

i.e.
$$\begin{pmatrix} x_1' \\ x_2' \\ x_3' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \quad (3.8)$$

$\{\epsilon \mid t\}$ represents a pure translation and $\{\alpha \mid 0\}$ denotes a rotation about the origin. Two transformations $\{\alpha \mid t\}$, $\{\beta \mid t'\}$ taken in succession, may be represented by (see (3.6))

$$x' = \alpha(\beta x + t') + t \quad (3.9)$$

i.e.
$$\{\alpha \mid t\}\{\beta \mid t'\} \equiv \{\alpha\beta \mid \alpha t' + t\} \quad (3.10)$$

The inverse of a transformation is that which returns the crystal to its original situation. This means that the product of an operator, with its inverse, must be equivalent to the identity operator. The inverse of $\{\alpha \mid t\}$ written $\{\alpha \mid t\}^{-1}$ is $\{\alpha^{-1} \mid -\alpha^{-1}t\}$ where α^{-1} is the inverse matrix of α. The inverse of the inversion operator $\{I \mid 0\}$ is itself. The same is true for the identity operator $\{\epsilon \mid 0\}$.

The effect of any operator on a function is to transform it into some other function. For example, the differential operator $\dfrac{d}{dx}$ changes x^2 into $2x$. It is necessary to define the effect of a Seitz operator on any arbitrary function. The operator is taken to be a substitutional one and its action on a function $f(r)$ is

$$\{\alpha \mid t\}f(r) = f(\{\alpha \mid t\}^{-1}r) \quad (3.11)$$

With this definition, the value of the function at each point in

space is left unaltered under the rotation or translation of the co-ordinate axes.

As an example illustrating equation (3.11), consider the two functions
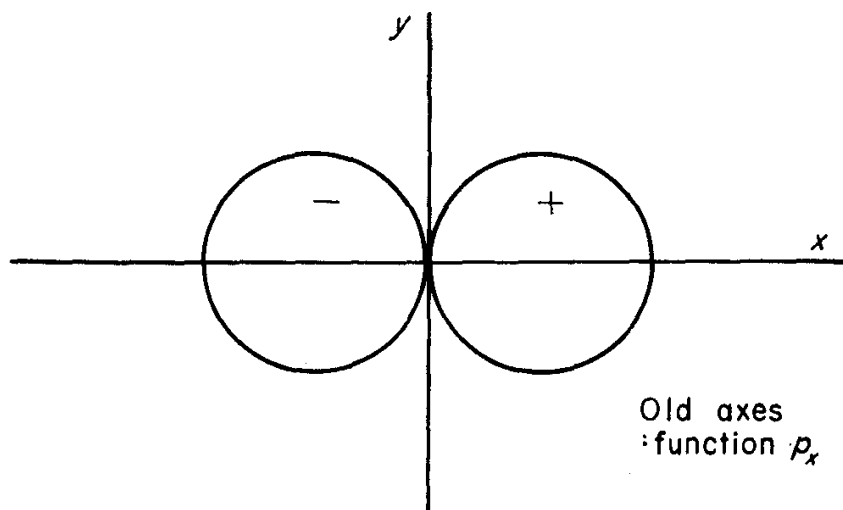
$$p_x = \cos\theta, \quad p_y = \sin\theta$$
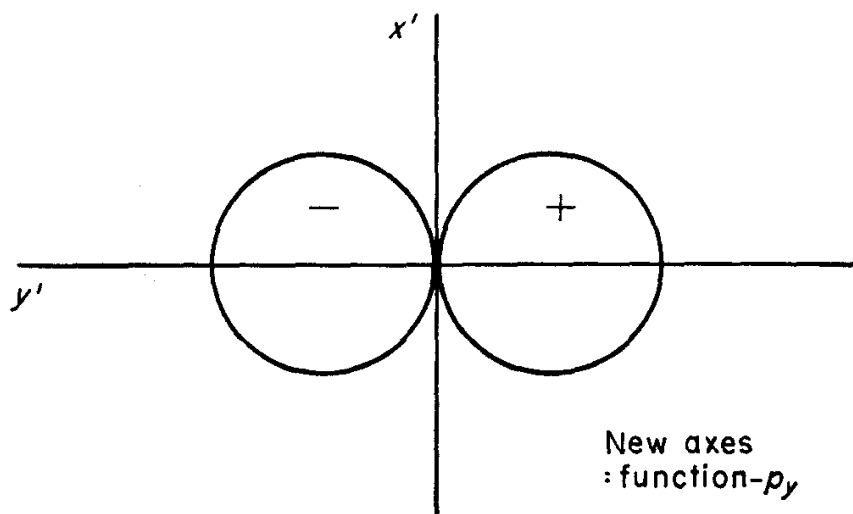
FIG. 3.6

FIG. 3.7

When the co-ordinate axes are rotated through $\pi/2$ radians about the z-axis in the anti-clockwise sense, the function p_x becomes $-p_y$ if the value of the function at each point in space remains unchanged.

50

The symbol representing the axis rotation may be written as $\{4_z \mid o\}$ and it has been shown above that

$$\{4_z \mid o\}p_x = -p_y$$

This result also follows from equation (3.11). The inverse of the operator $\{4_z \mid o\}$ represents a clockwise rotation of the axes through $\pi/2$ radians and

$$\{4_z \mid o\}p_x = \cos\left[\{4_z \mid o\}^{-1}\theta\right] = \cos\left(\theta + \frac{\pi}{2}\right) = -\sin\theta$$

Substitutional operators are linear

$$\{\alpha \mid t\}[a\psi_1(r) + b\psi_2(r)] = a\psi_1(\{\alpha \mid t\}^{-1}r) + b\psi_2(\{\alpha \mid t\}^{-1}r)$$
$$= a\{\alpha \mid t\}\psi_1(r) + b\{\alpha \mid t\}\psi_2(r), \qquad (3.12)$$

where a, b are complex constants.

The possession of symmetry by a body has important implications for the solutions of Schrödinger's equation.

For any physical system studied within the one-electron approximation, the Hamiltonian for an electron may be written

$$\mathscr{H}(x_1, x_2, x_3) = -\frac{\hbar^2}{2m}\nabla^2 + V(x_1, x_2, x_3) \qquad (3.13)$$

where spin-dependent terms are omitted. If the system undergoes some reflection, rotation or translation, then the old co-ordinates x_1, x_2, x_3 must be replaced by new co-ordinates x_1', x_2', x_3' as defined by an expression of the form (3.4). It is shown in standard textbooks on the calculus, that the Laplacian operator ∇^2 is invariant under such a linear transformation.

i.e.

$$\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} = \frac{\partial^2}{\partial x_1'^2} + \frac{\partial^2}{\partial x_2'^2} + \frac{\partial^2}{\partial x_3'^2} \qquad (3.14)$$

If the change in co-ordinates corresponds to a 'symmetry operation', then the system is brought into self-coincidence by such an operation, and it is quite clear that the potential function is also invariant under the transformation.

As an illustration, consider the potential which an electron

experiences when moving in the field of two protons. This occurs in the hydrogen molecular ion.

One of the symmetry operations which brings the physical system into self-coincidence, is a rotation through 180° about any axis perpendicular to, and bisecting, the line joining the two protons. Suppose the arbitrary point P is rotated into P' by
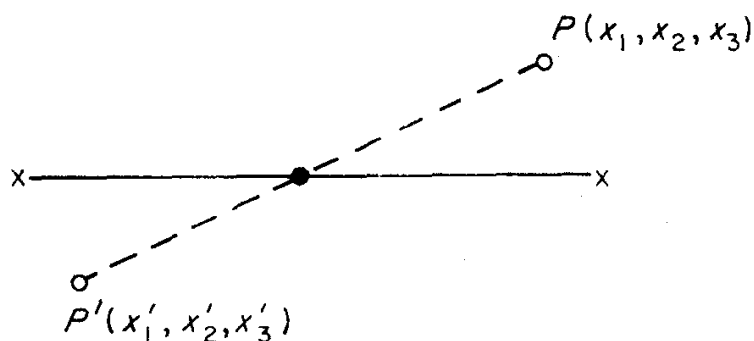

FIG. 3.8

such an operation. It is obvious that the potential function has the same value at P and P',

i.e. $$V(x_1, x_2, x_3) = V(x_1', x_2', x_3') \qquad (3.15)$$

The co-ordinates (x_1, x_2, x_3) of P are related to those of $P'(x_1', x_2', x_3')$ by a transformation of the form (3.3). This transformation may be interpreted as a rotation of co-ordinate axes instead of as a physical rotation. Equation (3.15) expresses the result that the potential function is invariant when the transformation is applied.

The whole Hamiltonian is, in fact, invariant under a symmetry transformation. This basic result is of the utmost importance in the application of group theory to quantum mechanics, and is intimately related to the occurrence of degeneracies.

Suppose for a given physical system a wave function corresponds to an energy E, then

$$\mathscr{H}(x_1, x_2, x_3)\psi(x_1, x_2, x_3) = E\psi(x_1, x_2, x_3) \qquad (3.16)$$

If the system is symmetric in some sense, then the Hamil-

tonian will be invariant under some transformation of co-ordinates. If the equation (3.16) undergoes this transformation, then

$$\mathscr{H}(x_1', x_2', x_3')\psi'(x_1', x_2', x_3') = E\psi'(x_1', x_2', x_3') \quad (3.17)$$

The new Hamiltonian $\mathscr{H}(x_1', x_2', x_3')$ has the same functional form as the original, and so the differential equation (3.17) is basically equation (3.16). In general, the transformed function $\psi'(x_1', x_2', x_3')$ is not the same as $\psi(x_1, x_2, x_3)$ and they are two different wave functions denoting different states that solve the same equation, and belong to the energy E.

Perhaps these ideas can be clarified by considering the particular case of a free particle moving in one dimension. The energy eigenfunction e^{ikx} belongs to the energy $\hbar^2 k^2/2m$.

i.e.
$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} \right]e^{ikx} = \left(\frac{\hbar^2 k^2}{2m} \right)e^{ikx} \quad (3.18)$$

The Hamiltonian is invariant under the inversion through the origin, and so the transformed wave function e^{-ikx}, obtained by changing x into $-x$, belongs to the same energy as e^{ikx}. This result is, of course, trivial, and is obvious from the form of the energy function.

§ 3.3 Groups

Group theory involves two basic ideas, groups themselves, and function spaces.

A group is a set of elements {A}, which obey certain specified rules. In this book the elements will be taken to be transformation operators of the type (3.4), but the concept is more general. The members of a group have the following properties.

(1) It must be possible to combine the elements to form a new element of the group.

e.g.
$$A = BC \quad (3.19)$$

If the elements are transformation operators then (3.19) means that if the operator C is applied first, and B second, the result is equivalent to applying operator A alone, where A is another member of the group. The order of the operators is important. Consider a point P on the x-axis, together with two lines of symmetry, m_1 along the x-axis, and m_2 bisecting the angle between the positive x and y axes.
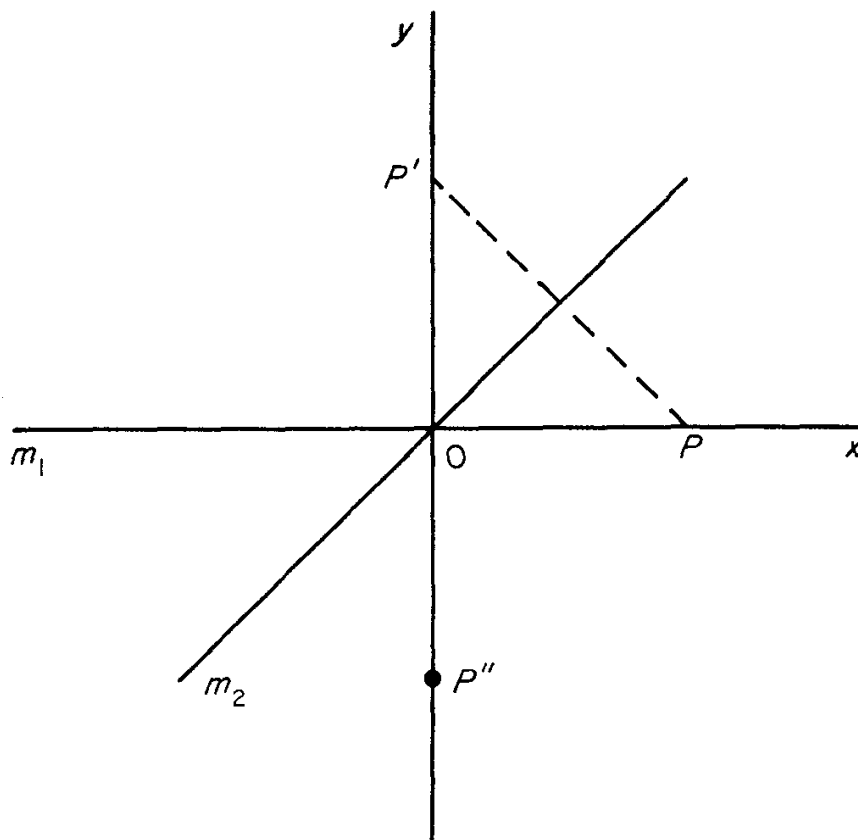

Fig. 3.9

If the operator m_1, is applied first, followed by m_2, then the point P moves to P'. Alternatively, if m_2 is applied first and followed by m_1, then the point P moves P''. The two operators m_1 and m_2 do not commute.

Conversely, any two rotations about the same axis do commute; in this case, the order in which the operations are carried out does not matter.

(2) One of the members of the group is a unit operator E

such that it commutes with all the other members of the group.

i.e. $$EA = AE = A \qquad (3.20)$$

If the elements are Seitz operators, the unit operator is $\{\epsilon \mid 0\}$.

(3) Every element A in a group has an inverse A^{-1} so that the combination of an operator with its inverse, results in the unit operator.

$$AA^{-1} \equiv A^{-1}A = E \qquad (3.21)$$

If A is the operator $\{\alpha \mid t\}$, its inverse is $\{\alpha^{-1} \mid -\alpha^{-1}t\}$.

(4) The combination of three operators must be uniquely defined.

i.e. $$A(BC) = (AB)C = ABC \qquad (3.22)$$

The square group

A simple example of a group of symmetry elements are those operations which leave a square invariant. It is assumed that the two plane sides of the square are not identical.
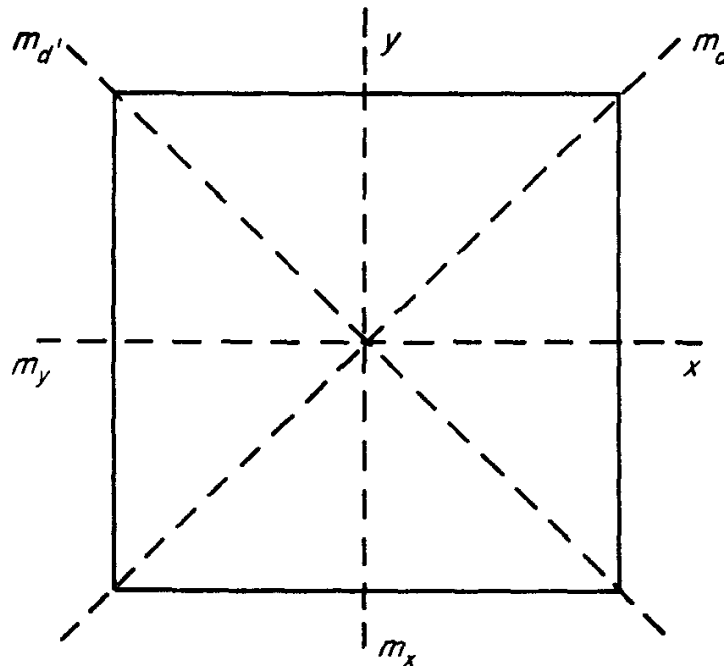
FIG. 3.10   The square group

There are eight symmetry operations which leave the square invariant, they are:

(a) The identity operator E.

(b) The two perpendicular mirror planes m_x, m_y.

(c) The two perpendicular mirror planes m_d, $m_{d'}$.

(d) The three rotations about the four-fold axis through o in the z-direction, 4_z, 2_z, 4_z^3 corresponding to rotations of 90°, 180° and 270° respectively.

These eight operations may be shown to form a group, and Table 3.2 is the 'multiplication table' for the group:

TABLE 3.2

Multiplication table for the group of the square 4mm

		E	m_x	m_y	m_d	$m_{d'}$	4_z	2_z	4_z^3	Applied first
	E	E	m_x	m_y	m_d	$m_{d'}$	4_z	2_z	4_z^3	
	m_x	m_x	E	2_z	4_z	4_z^3	m_d	m_y	$m_{d'}$	
	m_y	m_y	2_z	E	4_z^3	4_z	$m_{d'}$	m_x	m_d	
	m_d	m_d	4_z^3	4_z	E	2_z	m_y	$m_{d'}$	m_x	
	$m_{d'}$	$m_{d'}$	4_z	4_z^3	2_z	E	m_x	m_d	m_y	
	4_z	4_z	$m_{d'}$	m_d	m_x	m_y	2_z	4_z^3	E	
	2_z	2_z	m_y	m_x	$m_{d'}$	m_d	4_z^3	E	4_z	
Applied second	4_z^3	4_z^3	m_d	$m_{d'}$	m_y	m_x	E	4_z	2_z	

In Table 3.2, the elements in the top row are applied first and then the operation in the first column. For example, if the operation m_d is applied, and then followed by the rotation 4_z, then the result is equivalent to the reflection m_x. If 4_z is applied first and then m_d, the result is m_y. This illustrates a point already mentioned, that the order of the operations is important, as they do not necessarily commute.

Point groups

A 'point group' is a group of symmetry operations applied about a point which leave a body invariant. The group discussed above is of this type. In infinite crystals there are thirty-two allowed point groups. This means the point group at any point in a crystal must be one of these thirty-two possibilities. This restriction to thirty-two follows the consideration that a crystal lattice must have translational symmetry. For example, all point groups containing a five-fold axis, or any axis greater than six-fold, are excluded. Seven of the groups define the seven crystal systems. The lattice points of all the empty Bravais lattices in a given crystal system have the same point group. The remaining twenty-five point groups arise by associating arrangements of atoms with each lattice point.

If a basis of atoms is assigned to a lattice point in this way, the lattice point group will be reduced if the atomic arrangement has a lower symmetry than the Bravais lattice itself.

In a crystal, each point has an associated point group. There is an arrangement of point groups in space. Such an arrangement is called a 'space group'. There are two hundred and thirty allowed space groups in an infinite crystal. In addition to the point group symmetry elements, such as rotations and reflections, there is now the possibility of screw-axes or glide plane operations, which are composed of non-primitive translations, together with a rotation or reflection respectively. The full set of translation operators always forms a group of its own. It is said to form a sub-group of the full space group.

§ 3.4 Function spaces

The transformation operators act on functions, so it is necessary to introduce the concept of function spaces, to realize the potentiality of group theory. A function space is defined by a set

E

of linearly independent functions. A set of functions $\{\phi_i\}$ is said to be linearly independent if the relation

$$a_1\phi_1 + a_2\phi_2 + \ldots + a_n\phi_n = 0 \qquad (3.23)$$

implies that the constants $a_i = 0$ for all i. This means none of these functions can be expressed in terms of the others. Any set of mutually orthogonal functions are linearly independent. Conversely, if a set of non-orthogonal functions are linearly independent and are also quadratically integrable, it is always possible to form a mutually orthogonal set from them by a suitable linear transformation. Suppose $\{\phi_i\}$ is the non-orthogonal set, then an orthogonal set $\{\theta_i\}$ can be defined as follows. Let $\theta_1 = \phi_1$ and then choose α with $\theta_2 = \phi_2 + \alpha\theta_1$ so that θ_2 is orthogonal to θ_1. Then choose β_1, β_2 with $\theta_3 = \phi_3 + \beta_1\theta_1 + \beta_2\theta_2$ so that θ_3 is orthogonal to θ_1 and θ_2, etc. The set $\{\theta_i\}$ may then be normalized.

The function space defined by the orthogonal set of functions $\{\theta_i\}$ includes all functions of the type

$$b_1\theta_1 + b_2\theta_2 + \ldots + b_n\theta_n \qquad (3.24)$$

where b_i's are any complex constants. The number of linearly independent functions used to define the space, gives the dimensionality. It is clear that either of the sets $\{\phi_i\}$ and $\{\theta_i\}$ define the same space. This definition is in accordance with the usual idea of Cartesian space. The unit vectors $\hat{e}_1$, $\hat{e}_2$ and $\hat{e}_3$ are orthogonal vectors and are also linearly independent. Together, they define a three-dimensional space which includes all vectors of the type

$$\boldsymbol{r} = c_1\hat{e}_1 + c_2\hat{e}_2 + c_3\hat{e}_3 \qquad (3.25)$$

The relationships between the function spaces and the transformation operators is very important. The function space $\{\theta_i\}$ is said to be invariant under the set of operators $\{A\}$ if all transformed functions of the type $A\theta_i$ belong to the space. The Cartesian vector space, defined by the unit vectors $\{\hat{e}_i\}$ is invariant under any point group.

The space $\{\theta_i\}$ is said to be irreducible under the set of

operators {A} if with any function x_i in the space, the set of transformed functions {Ax_i} defines the same space where A runs over all the members of {A} in turn. The Cartesian space {$\hat{e}_i$} is irreducible under the set of three operators consisting of a rotation of 90° about the x-axis and 90° about the y-axis and 90° about the z-axis.

On the other hand, this Cartesian space is not irreducible under the set of operators consisting of the identity and rotations of ±120° about the (111) axis. To see this, consider the unit vector along the (111) axis.

The space defined by the functions {ψ_i} is said to be a sub-space of the function space {θ_i} if every function in the sub-space belongs to the space {θ_i} and if the converse is not true. The plane defined by the unit vectors $\hat{e}_1$, $\hat{e}_2$ is a sub-space of the three-dimensional space given by $\hat{e}_1$, $\hat{e}_2$, $\hat{e}_3$. All the vectors in the sub-space are of the type

$$r = c_1\hat{e}_1 + c_2\hat{e}_2 \qquad (3.26)$$

and obviously belong to the full Cartesian space. Alternatively, any vector including $\hat{e}_3$, while belonging to the three-dimensional space, does not belong to the sub-space.

Matrix representations

If a function space {θ_i} is invariant under the action of a group of operators {A} then the transformed functions may be expressed in terms of the original set.

i.e.
$$A\theta_i = \sum_m \alpha_{mi}\theta_m \qquad (3.27)$$

The matrix (α_{mi}) represents the effect of the operator A on the basis functions {θ_i}. Each of the operators in the set has a matrix representation. If B is another operator in the set, then

$$B\theta_i = \sum_m \beta_{mi}\theta_m \qquad (3.28)$$

The effect of the multiple operator AB can be seen to be

$$AB\theta_i = \sum_j \sum_m \alpha_{jm}\beta_{mi}\theta_j \qquad (3.29)$$

if the operators are linear.

The matrix corresponding to the product AB is the product of the separate matrices representing A and B. The matrices obey the same group multiplication table as the operators themselves, and are said to form a representation of the group. The order of the matrices gives the dimensionality of the representation.

A different set of functions $\{\theta_i'\}$ can be used to define the same vector space as $\{\theta_i\}$, if the new basis functions can be expressed in the terms of $\{\theta_i\}$ by some linear transformation.

$$\theta_j' = \sum_i S_{ij}\theta_i \tag{3.30}$$

and conversely

$$\theta_j = \sum_i S_{ij}^{-1}\theta_i' \tag{3.31}$$

The action of a transformation operator on θ_j', is given by

$$A\theta_j' = \sum_i A S_{ij}\theta_i = \sum_i \sum_m S_{ij}\alpha_{mi}\theta_m$$
$$= \sum_k \sum_i \sum_m S_{km}^{-1}\alpha_{mi}S_{ij}\theta_k' \tag{3.32}$$

The new basis functions transform according to the representation

$$S^{-1}\alpha S \tag{3.33}$$

This new representation is said to be equivalent to the representation α. A change of the basis function as described above, is equivalent to choosing a new set of unit vectors $\{\hat{e}_i'\}$ in Cartesian space related to the old set $\{\hat{e}_i\}$ by some rotation.

The matrices in equivalent representations corresponding to a given operator, need not be identical, but their traces, that is the sum of diagonal elements, are identical.

$$\sum_i [S^{-1}\alpha S]_{ii} = \sum_m \sum_j \sum_i S_{im}^{-1}\alpha_{mj}S_{ji} = \sum_m \sum_j \sum_i S_{ji}S_{im}^{-1}\alpha_{mj}$$
$$= \sum_m \sum_j \delta_{jm}\alpha_{mj}$$
$$= \sum_j \alpha_{jj} \tag{3.34}$$

A set of matrices representing a group of transformation operators with respect to a set of basis functions $\{\theta_i\}$, is said to

form an irreducible representation if the function space defined by $\{\theta_i\}$ is irreducible under the group of operators. A reducible representation can always be brought into irreducible form by an equivalence transformation of the type (3.33).

The reducible matrices representing all the elements of the group are then reduced to block form, all with the same block structure. That is, each matrix is a direct sum of square matrices a_1, a_2, . . . along the leading diagonal and the dimensions of corresponding sub-matrices are the same for every operator in the group.

e.g.

$$\begin{pmatrix} a_1 & 0 & 0 \\ \hline 0 & a_2 & 0 \\ \hline 0 & 0 & a_3 \end{pmatrix}$$

A set of sub-matrices forms one of the constituent irreducible representations of the group.

The functions xe^{-r}, ye^{-r}, ze^{-r} correspond to a reducible representation for the square point group. (Table 3.2 and Fig. 3.10.)

The matrices representing the different transformation operators are given in Table 3.3. As an example, consider the effect of applying the operator m_x, the mirror reflection through a plane perpendicular to the x-axis.

$$m_x(xe^{-r}, ye^{-r}, ze^{-r}) = (xe^{-r}, ye^{-r}, ze^{-r}) \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$(3.35)$$

On closer inspection it will be observed that none of the eight group elements mixes the functions xe^{-r}, ye^{-r} with ze^{-r}. In fact, the two sets (xe^{-r}, ye^{-r}) and (ze^{-r}) span separate spaces which are invariant under the square point group. The two separate irreducible representations are listed in Table 3.3 under A and E.

The letters A, B are commonly used to label one-dimensional representations, E is used for a two-dimensional representation and T is used for a three-dimensional representation.

TABLE 3.3

Matrix representations for the square group 4 mm

	E	m_x	m_y	m_d	$m_{d'}$	4_z	2_z	4_z^3
	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
$ze^{-r}A$	1	1	1	1	1	1	1	1
$\left.\begin{array}{l} xe^{-r} \\ ye^{-r} \end{array}\right\}E$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$
$\left.\begin{array}{l} (x+iy)e^{-r} \\ (x-iy)e^{-r} \end{array}\right\}E$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$

(Note, the active rotation 4_z^3 corresponds to the passive rotation 4_z (see page 51).)

In this simple instance, there was no need to carry out an equivalence transformation to bring the matrices into the characteristic 'block' form.

All groups have one identity representation, such as A, in which all the 'matrices' are unity. This representation is not faithful in that the representation possesses more relations than the group itself. (Compare Table 3.2 with Table 3.3.)

There are other irreducible representations of the square point group apart from A and E. Altogether there are five irreducible representations of the square point group, four one-dimensional, and one two-dimensional representations. The trace of a matrix corresponding to an operator is called the 'character' of the operator in the representation, and is independent of the choice of basis functions (3.34). Table 3.4 is a character table for the square point group and includes all the irreducible representations.

Another basis for the irreducible representation E is $(x + iy)e^{-r}$, $(x - iy)e^{-r}$. Clearly these functions are a simple linear combination of the previous basis and produce an equivalent representation of the square groups. The transformation matrix is

$$S = \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} \quad \text{and} \quad S^{-1} = \tfrac{1}{2}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix}$$

The new matrices are listed in Table 3.3 and are related to the old by (3.33).

e.g. for m_x

$$\tfrac{1}{2}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix}\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

The group characters are the same for both sets of basis functions and are given in the last row of Table 3.4.

The reduction of a space into sub-spaces defined by sets of functions forming irreducible representations for the group considered, can always be done, and is of the utmost importance in the application of group theory to quantum mechanics. The concept of symmetry class is useful in this context.

The elements of a group may be divided into distinct sets called 'classes'. Given any element A of a group, then the set of

TABLE 3.4

Character table for square point group

$4\,mm$	E	m_x	m_y	m_d	$m_d{}'$	4_z	2_z	$4_z{}^3$
A_1	1	1	1	1	1	1	1	1
A_2	1	−1	−1	−1	−1	1	1	1
B_1	1	1	1	−1	−1	−1	1	−1
B_2	1	−1	−1	1	1	−1	1	−1
E	2	0	0	0	0	0	−2	0

elements $B^{-1}AB$, as B runs over all elements in the group, is called a class.

The operation $B^{-1}AB$, is the net result obtained by first rotating the system to some equivalent position by B, next carrying out the operation A, and then reversing the initial operation by B^{-1}. The members of a class must be operators of the same sort, such as rotations through the same angle, but performed about different axes which are related to each other by members of the group.

The characters of all the elements of a class in a given representation are obviously identical (3.34). In a group character table it is necessary only to specify the classes. In Table 3.4 there are five classes

$$E$$
$$m_x,\ m_y$$
$$m_d,\ m_d{}'$$
$$4_z,\ 4_z{}^3$$
$$2_z$$

The number of classes in a group is equal to the number of irreducible representations. For the square point group, there are five classes and five irreducible representations. If n_i is the dimensionality of an irreducible representation, and N is the

number of elements in the group, then the following relation can be derived:

$$\sum_i n_i{}^2 = N \qquad (3.36)$$

The sum is over all the possible irreducible representations. If the number of classes in a group is known, and if the number of elements in a group is also known, then using (3.36) the dimensionality of the irreducible representations can be found.

For the square point group, the number of classes, and hence the number of irreducible representations, is five.

There are eight elements in the point group, and from (3.36),

$$2^2 + 1^2 + 1^2 + 1^2 + 1^2 = 8 \qquad (3.37)$$

There are four one-dimensional and one two-dimensional irreducible representations for the group as shown in the Table 3.4.

The relation (3.36) has important consequences for Abelian groups. An Abelian group is one in which all the elements commute with one another. The elements which compose a four-fold rotation axes form such a group. Each element in an Abelian group forms a class in itself. This means the number of irreducible representations is equal to the number N of elements in the group. From the equation (3.36), it is obvious that all these irreducible representations must be one-dimensional. This result is referred to again in Chapter 5 with regard to the Bloch theorem.

Sufficient background knowledge will now have been gained by the reader concerning the theory of groups and their representations. The next step is to relate the group theory to quantum mechanics.

§ 3.5 Symmetry and quantum mechanics

Section 3.2 has shown that there is a close link between the occurrence of degeneracies and symmetry operators. If $\psi_1(r)$ is a solution of some Hamiltonian $\mathcal{H}$, then

$$\mathcal{H}\psi_1(r) = E\psi_1(r) \qquad (3.38)$$

If the Hamiltonian is invariant under the transformation operator A then

$$A\mathscr{H} = \mathscr{H}$$

Operating with A on the left side of equation (3.38), $\mathscr{H}$ and A commute.

$$A\mathscr{H}\psi_1 = \mathscr{H}A\psi_1$$

The transformed wave function

$$A\psi_1 = \psi_2$$

is also a solution of the Hamiltonian, corresponding to the same energy.

If ψ_1 and ψ_2 are linearly independent, they represent degenerate eigenfunctions.

Corresponding to each energy level there is a set of degenerate eigenfunctions, which span a space which is invariant under the action of any group of transformation operators which commute with the Hamiltonian. The eigenfunctions produce some representation of the group. The basic theorem relating group theory to quantum mechanics postulates that the set of all degenerate wave functions corresponding to a given energy level, forms an irreducible representation of the group of all the operators which commute with the Hamiltonian.

In general, this statement is true, but sometimes it happens that non-equivalent irreducible representations correspond to the same energy. This occurrence is termed an 'accidental degeneracy'.

For a multi-electron wave function, account must be taken of the permutation operators which commute with the multi-electron Hamiltonian. This additional complication does not arise in the one-electron approximation.

It is a well-known fact that when a physical system is perturbed, degeneracies are often destroyed. This is easily understood if it is observed that in general, the perturbed Hamiltonian possesses a lower symmetry than that which is unperturbed. The erstwhile degenerate wave functions will now form

a reducible representation for the new smaller symmetry group, and will split into two or more irreducible representations. Hence a degenerate level may be expected to divide into two or more levels of diminished degeneracy.

§ 3.6 Some applications of group theory

Axial rotation group

The group composed of all the rotations about some axis is called the axial rotation group. If all angles of rotation are allowed, the group has an infinite number of elements. The group is Abelian, since a rotation ϕ_1, followed by ϕ_2, is exactly equivalent to ϕ_2 followed by ϕ_1. Each rotation forms a class in itself, and so all the irreducible representations are one-dimensional. The representation must satisfy

$$\Gamma(\phi_1)\Gamma(\phi_2) = \Gamma(\phi_1 + \phi_2)$$

The solutions of this equation are

$$\Gamma^{(m)}(\phi) = e^{im\phi}$$

The index m is restricted to the values

$$m = 0, \pm 1, \pm 2, \ldots$$

by the requirement that

$$\Gamma^{(m)}(2\pi) = \Gamma^{(m)}(0) = 1$$

The basis functions for these irreducible representations are of the form

$$\psi_m(r, \theta, \phi) = f(r, \theta)e^{im\phi} \quad m = 0, \pm 1, \pm 2, \ldots$$

The eigenfunctions for a Hamiltonian whose symmetry group is the group of all rotations about an axis, are of this type. This expresses the result that angular-momentum is conserved along an axis of symmetry.

Three protons positioned at the vertices of an equilateral triangle

The Hamiltonian for a single electron moving in the field of three protons arranged in the form of an equilateral triangle is

$$\mathscr{H} = -\frac{\hbar^2}{2m}\nabla^2 + \left[\frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} + \frac{e^2}{|\mathbf{r} - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{r} - \mathbf{r}_3|}\right]\frac{1}{4\pi\epsilon_0}$$

where $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$ denote the positions of the protons.
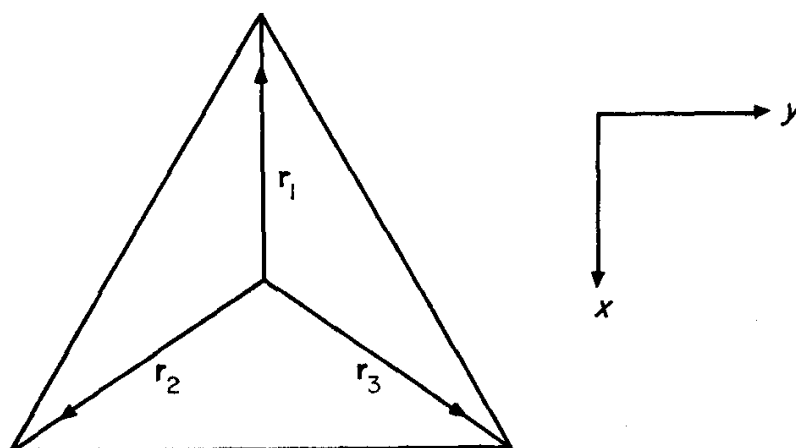
The origin is at the centre of the triangle

FIG. 3.11   The group of the equilateral triangle

This system is not of any great importance in itself, but the symmetry is related to that of an ion surrounded by three molecules of water in the hydrated crystal of a salt. (The ozone molecule has almost this symmetry.)

There are twelve symmetry operations which leave the system of three protons invariant and they form the group $\bar{6}m2$. They are:

(*a*) the identity operation E;

(*b*) the three mirror planes of the type m_y;

(*c*) the three rotations of the type 2_x through 180° about the vectors $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$ respectively;

(*d*) the mirror plane m_z perpendicular to the z-axis and including all three protons;

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(e) the two rotations 3_z, 3_{z^3} corresponding to a positive rotation of 120° and 240° about the z-axis respectively;

(f) the two operations $\bar{6}_z$ involving a rotation through 60° and 300° about the z-axis followed by an inversion through the origin.

TABLE 3.5

Character table for the point group $\bar{6}m2$

Number of elements in class	I	3	3	I	2	2
Particular element in class	E	m_y	2_x	m_z	3_z	$\bar{6}_z$
Representation						
A_1'	I	I	I	I	I	I
A_2'	I	−I	−I	I	I	I
A_1''	I	−I	I	−I	I	−I
A_2''	I	I	−I	−I	I	−I
E'	2	0	0	2	−I	−I
E''	2	0	0	−2	−I	I

The point group $\bar{6}m2$ is composed of six classes, so there are six irreducible representations of the group. This observation, together with the equation 3.36 determines the dimensions of the representations.

$$1^2 + 1^2 + 1^2 + 1^2 + 2^2 + 2^2 = 12$$

There are four one-dimensional and two two-dimensional irreducible representations of the group.

The eigenfunctions of the Hamiltonian belonging to the same energy must form a basis for one of the representations. It is to be expected that the ground state has the maximum symmetry, and so the state is non-degenerate and the eigenfunction is a basis of the representation A_1'. The function z^2 has this symmetry.

The hydrogen atom in an electric field with symmetry $\bar{6}m2$

In this section is considered the effect of an electric field with symmetry $\bar{6}m2$ on the degenerate $(2p)$ level of the hydrogen atom.

Before the electric field is applied, the single hydrogen electron moves in the spherically symmetrical field due to the 'fixed' proton.

The electron Hamiltonian is invariant under all rotations about any axis through the proton taken at the origin;

    i.e. the Hamiltonian is invariant under the full rotation group.
The $(2p)$ states

$$(2p_x) = f(r)x, \quad (2p_y) = f(r)y, \quad (2p_z) = f(r)z$$

with $f(r)$ a function of r only, transform according to an irreducible representation of this group and belong to the same energy. The $(2p)$ level is triply degenerate if spin degeneracy is ignored.

It is quite clear by inspection of Table 3.5 that when the electric field is applied and the electron Hamiltonian has the reduced symmetry $\bar{6}m2$ then at most a double degenerate level remains. The three $(2p)$ wave functions transform according to a reducible representation of the group $\bar{6}m2$ which is given in Table 3.6.

<div align="center">

TABLE 3.6

	E	m_y	2_x	m_z	3_z	$\bar{6}_z$
p_x, p_y, p_z	3	$+1$	-1	$+1$	0	-2

</div>

This representation is composed of the two irreducible representations A_2'' and E'.

The previously triply degenerate $(2p)$ level has split up into a single level and a doubly degenerate level under the action of the electric field.

A similar type of argument is used in 'crystal field theory' problems.

Problems for Chapter 3

1. Let a_1, a_2 and a_3 be a particular set of basis vectors for some three-dimensional Bravais lattice. Define three vectors u_1, u_2 and u_3 by

$$u_1 = l_1 a_1 + m_1 a_2 + n_1 a_3$$
$$u_2 = l_2 a_1 + m_2 a_2 + n_2 a_3$$
$$u_3 = l_3 a_1 + m_3 a_2 + n_3 a_3$$

where l_1, m_1, ... m_3, n_3 are integers. The condition that these vectors form a new basis is

$$a_1 = r_1 u_1 + s_1 u_2 + t_1 u_3$$

with r_1, s_1, t_1 integers and similarly for a_2 and a_3. Show that this condition is satisfied if the determinant

$$\begin{vmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{vmatrix} = \pm 1$$

Verify that the primitive cell volume remains constant under the change of basis.

2. (a) Show that there is a two-fold axis going through every lattice point of a two-dimensional Bravais net.

(b) Show that if a Bravais net has an axis of n-fold symmetry about some arbitrary point it has at least an axis of n-fold symmetry about any lattice point. (Hint — Consider the fundamental rotation about the arbitrary point P which takes the lattice points A and B to B and C respectively. Then apply the translation which returns A to its original position and note the final position of B.)

3. Prove that a Bravais net can only have an axis of two-, four- or six-fold symmetry, about a lattice point. Show also that a three-fold axis may exist at an arbitrary point. (Hint — Use the results of Problem 2 and consider the fundamental rotation of the shortest possible basis vector a_1 about a lattice point.)

4. Prove that the elements of the rotation transformation matrix (see equations (3.5) and (3.7))

$$\begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{pmatrix}$$

satisfy the relations

$$\sum_{j=1}^{3} \alpha_{ij}{}^2 = 1 \quad \text{for all } i$$

$$\sum_{i=1}^{3} \alpha_{ij}\alpha_{im} = 0 \quad j \neq m$$

Prove also that the determinant of the transformation matrix is ± 1.

5. Describe the four symmetry operations under which a rectangle is invariant. It may be assumed that the two faces of the rectangle are not identical.

Draw up a group multiplication table. (This is the group 2mm.)

6. Describe the six symmetry operations under which an equilateral triangle is invariant. It may be assumed that the two faces of the triangle are not identical. Draw up a group multiplication table. (This is the group 3m and is a sub-group of the group $\bar{6}m2$ studied in the text.)

7. The permutations of n objects form a group. This is called the 'symmetric group'. There are six permutations of the objects 1, 2, 3. A permutation that replaces 1 by 2, 2 by 1, and leaves 3 invariant may be denoted by the symbol

$$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix}$$

The product of two such permutations is another of the six possible permutations.

e.g. $$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}\begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}$$

Draw up a group multiplication table for these permutations.

Show that this table can be made to have the same form as that of the group 3*m* of question six by pairing off each of the elements of the permutation group with a suitable element of the group 3*m*. The two groups are said to be 'isomorphic'. (Since all electrons are identical, a many-electron Hamiltonian is invariant under the group of permutations of the electron co-ordinates.)

8. The Hermitian adjoint A^+ of a real operator A may be defined by

$$\int (A\phi^*)\psi \, d\tau = \int \phi^* A^+ \psi \, d\tau$$

where ϕ, ψ are arbitrary functions and the integration is over all space. If A is a linear operator which possesses an inverse A^{-1}, it is said to be a unitary operator if $A^+ = A^{-1}$.

A change of co-ordinate axes can not affect the values of the integral over all space $\int \phi^* \psi \, d\tau$. That is, the integral is invariant under a symmetry transformation of the type $\{\alpha \mid R_n\}$. Explain how this implies that $\{\alpha \mid R_n\}$ is a unitary operator.

9. (*a*) Show that the function space (x^2, y^2, $x^2 + y^2$) has the dimension two and not three.

(*b*) Similarly show that the function space (xy, yz, zx, $x(y-z)$) has dimension three and not four.

10. Describe the 48 symmetry operations which leave a cube invariant. These form the full cubic point group $m3m$. Divide the elements into the ten classes. Find the dimensions of all the irreducible representations.

11. List the 24 symmetry operations which leave a tetrahedron invariant. This is the point group $4\bar{3}m$. Divide the elements into the five classes and give the dimensions of all the irreducible representations.

(The carbon atom site in the methane molecule CH_4 and in the diamond lattice has the symmetry of this point group.)

12. In Chapter 3 it was shown that there are eight elements in the square point group $4mm$. The group character table is given below.

F

No. of elements in class	I	I	2	2	2
Typical element in class	E	2_z	4_z	m_x	m_d
Irreducible representation					
A_1	I	I	I	I	I
A_2	I	I	I	$-$I	$-$I
B_1	I	I	$-$I	I	$-$I
B_2	I	I	$-$I	$-$I	I
E	2	$-$2	0	0	0

The character of the group element A in the α-irreducible representation is denoted by $\chi^{(\alpha)}(A)$. Verify the 'orthogonality relations'.

$$\sum_A \chi^{(\alpha)*}(A)\chi^{(\beta)}(A) = 0 \qquad \alpha \neq \beta$$

$$\sum_A \chi^{(\alpha)*}(A)\chi^{(\alpha)}(A) = N$$

The summation is over all the N elements in the group.

13. The identity E and the two-fold rotation 2_z form the group 2. The character table is

	E	2_z
A	I	I
B	I	$-$I

A projection operator may be defined as

$$O^{(\alpha)} = \sum_A \chi^{(\alpha)}(A)A$$

where the sum is over all the operators in the group and $\chi^{(\alpha)}(A)$ is the character of A in the α-irreducible representation. The effect of this operator on an arbitrary function $f(x)$ is to 'project' out that part which transforms according to the α-representation.

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Apply the projection operator method to the function $f(x)$ and obtain functions which transform according to the representations A and B of the group 2.

14. The functions (xy, xz, yz) define a three-dimensional function space. By the projection operator technique pick out those functions in this space which transform according to the irreducible representations B_2 and E of the square point group $4mm$. (See Problem 12.)

15. The atomic orbitals $(2s)$, $(2p_x)$, $(2p_y)$ and $(2p_z)$ form the basis for a reducible representation of the tetrahedral point group $\bar{4}3m$. (See Problem 11.) Find five matrices of this representation each corresponding to a group element from one of the five classes. Show that this representation is composed of a single one-dimensional and one three-dimensional irreducible representations. (Hint — Choose the co-ordinate axes so that a 3-fold axis lies along the (111) direction). (The $(2s)$, $(2p_x)$, $(2p_y)$, $(2p_z)$ carbon atomic functions are available for bond formation in the CH_4 molecule.)

16. Consider an electron moving in the field of four protons positioned at the vertices of a tetrahedron. An eigenfunction of the Hamiltonian must be associated with one of the five irreducible representations of the tetrahedral point group $\bar{4}3m$. (See Problems 11 and 15.) A uniform electric field is applied along one of the three-fold tetrahedron axes from the centre to a vertex. The reduced symmetry group is the point group $3m$ composed of six elements. The group character table is given below.

No. of elements in class		2	3
Element in class	E	A	B
A_1	1	1	1
A_2	1	1	-1
A_3	2	-1	0

Identify the elements A and B.

The three atomic functions p_x, p_y, p_z form a basis for an irreducible representation of the tetrahedral group. (Problem 15.) Show that this representation is composed of two irreducible representations of the new symmetry group $3m$.

17 (a) For a real Hamiltonian the process of taking the complex conjugate commutes with $\mathscr{H}$.

i.e.
$$(\mathscr{H}\phi)^* = \mathscr{H}^*\phi^* = \mathscr{H}\phi^*$$

This is an additional operation which may produce degeneracies between eigenfunctions that belong to different representations that are irreducible under the symmetry group of the Hamiltonian. This operation of complex conjugation may be denoted by K. Show that K is not a linear operator but has a similar property, and also that

$$\left| K\int \phi^*\psi \, d\tau \right| = \left| \int \phi^*\psi \, d\tau \right|$$

K is said to be anti-linear and anti-unitary. What is the inverse of K?

(In the general case of a many particle Hamiltonian involving spin, the corresponding operator is the time-reversal operator T.)

(b) Suppose a uniform electric field is applied to a hydrogen atom. The eigenfunctions of the new Hamiltonian transform according to the representations of the axial rotation group ∞. In Chapter 3 these irreducible representations were shown to be one-dimensional. Explain why the new energy levels need not all be non-degenerate. (This is not a true example of extra degeneracy arising from K as it is also a consequence of the group ∞m, composed of all reflection planes through the axis of symmetry.)

Recommended further reading

Heine, V., *Group Theory in Quantum Mechanics*, Pergamon Press, London (1960).

Johnston, D. F., 'Group Theory in Solid State Physics'. Reports on Progress in Physics, XXIII, 66, 1960.

Tinkham, M., *Group Theory and Quantum Mechanics*, McGraw-Hill, New York (1964).

4

The Theory of Lattice Vibrations

§ 4.1 Longitudinal waves in continuous media

The atoms in a real crystal are never actually at rest. In this chapter the elastic vibrations of solids are discussed. For wavelengths that are large compared with the interatomic spacing, the crystal may be regarded as a continuous distribution of matter.

A longitudinal wave is one in which the particle displacement ζ is in the direction of wave propagation. The equation of motion of such waves in a continuous medium (Coulson 'Waves') is for propagation along the x-axis

$$\frac{\partial^2 \zeta}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \zeta}{\partial t^2} \quad \text{where} \quad c^2 = \frac{\lambda}{\rho} \tag{4.1}$$

λ is a constant of elasticity and ρ is the density. The general solution of this one-dimensional wave equation is

$$f(x - ct) + g(x + ct) \tag{4.2}$$

where f, g are arbitrary twice differentiable functions of x and t. The constant c is the velocity of all the waves. Particular solutions are the harmonic waves $\exp i(\omega t \pm kx)$ with $c = \omega/k$.

In addition to the longitudinal waves there are two types of transverse waves which are propagated with a velocity which is less than c. Of course the distinction into longitudinal and transverse waves can only strictly be made in an isotropic medium.

§ 4.2 Classical theory of lattice waves

When the wavelength of the elastic waves is of the order of the interatomic spacing it is clear that the microscopic structure of the crystal must be important. In a crystal the waves are transmitted by the vibrations of the atoms. The binding force between atoms can arise in several ways. For ionic crystals the force of attraction is the Coulomb field, for metals it is due to the free electrons and for valence crystals it is the covalent bond. When the atoms approach each other closely, short-range repulsive forces become dominant and prevent the collapse of the lattice.

Wave motion along a line of identical atoms

To a first approximation the force between any two atoms is proportional to their relative displacement from their equilibrium separation. Several important effects such as thermal expansion and heat resistivity are due to deviations from this. Nevertheless it is instructive to study the transmission of longitudinal waves down a line of atoms within this approximation. An additional simplification is to consider nearest neighbour interactions only.

Consider a line of identical atoms, each of mass m, which are a distance a apart in their equilibrium positions. x_n denotes the displacement of the nth atom from its equilibrium position. The resultant force (positive when acting to right) on the nth atom is

$$F_n = \alpha(x_{n+1} - x_n) - \alpha(x_n - x_{n-1}) \qquad (4.3)$$

where α is an elastic constant. The equation of motion is

$$m\ddot{x}_n = \alpha(x_{n+1} + x_{n-1} - 2x_n) \qquad \ddot{x}_n \equiv \frac{\mathrm{d}^2 x_n}{\mathrm{d}t^2} \qquad (4.4)$$

There exist travelling wave solutions in which the atoms vibrate with the same frequency and for these

$$x_n = A e^{i(\omega t + kna)} \qquad (4.5)$$

k is called the wave 'vector'. A is a complex constant, but it is
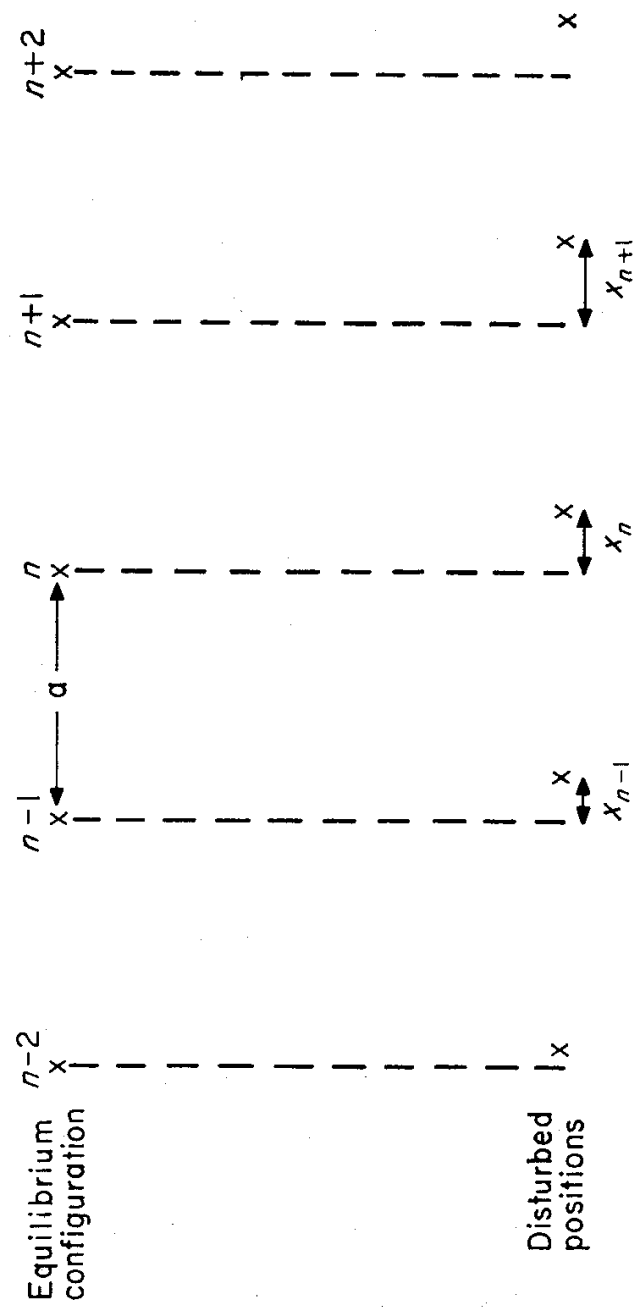
FIG. 4.1   A line of identical atoms
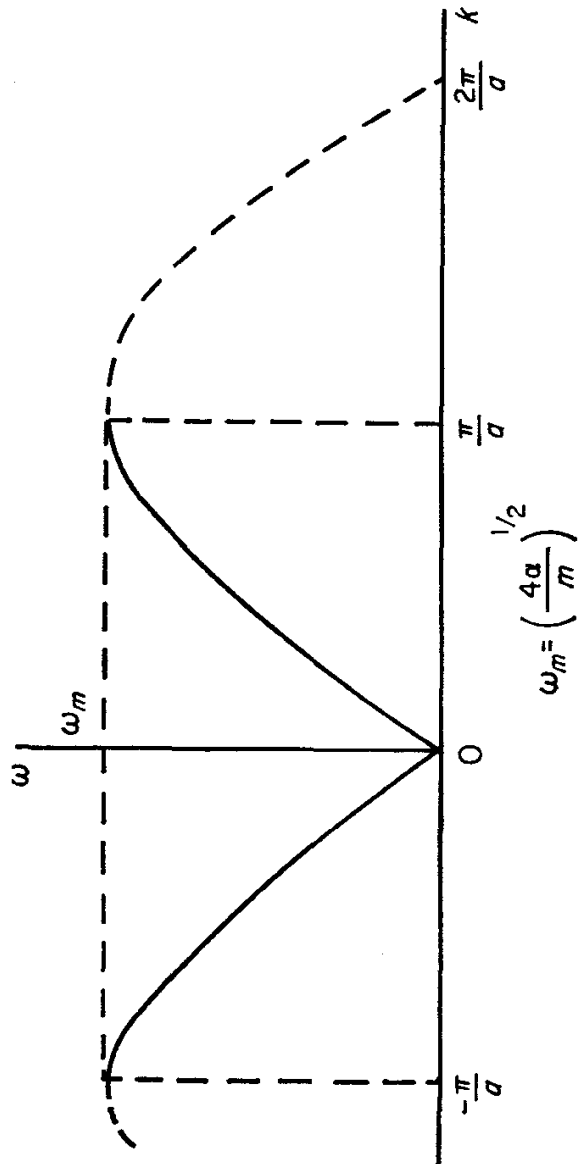
FIG. 4.2 Dispersion curve for linear lattice

understood that the real part of the r.h.s. is intended. Substitution of (4.5) into (4.4) gives

$$\omega = +\left(\frac{4\alpha}{m}\right)^{\frac{1}{2}}\left|\sin\frac{ka}{2}\right| \qquad (4.6)$$

Equation (4.6) is the dispersion relation between the angular frequency ω and the wave vector k. As ω is a periodic function in k with period $2\pi/a$ then for a given frequency there are an infinite number of k-values such that

$$k_m = k' + m\frac{2\pi}{a} \qquad m \text{ integer} \qquad (4.7)$$

with $|k'| \leqslant \pi/a$. From equation (4.5) it is quite clear that each of the k-values related by (4.7) represent the same atomic displacements and are therefore equivalent. This is explained when it is remembered that the wave description is here employed only to describe the motion of a discrete set of points rather than a continuous line of matter.
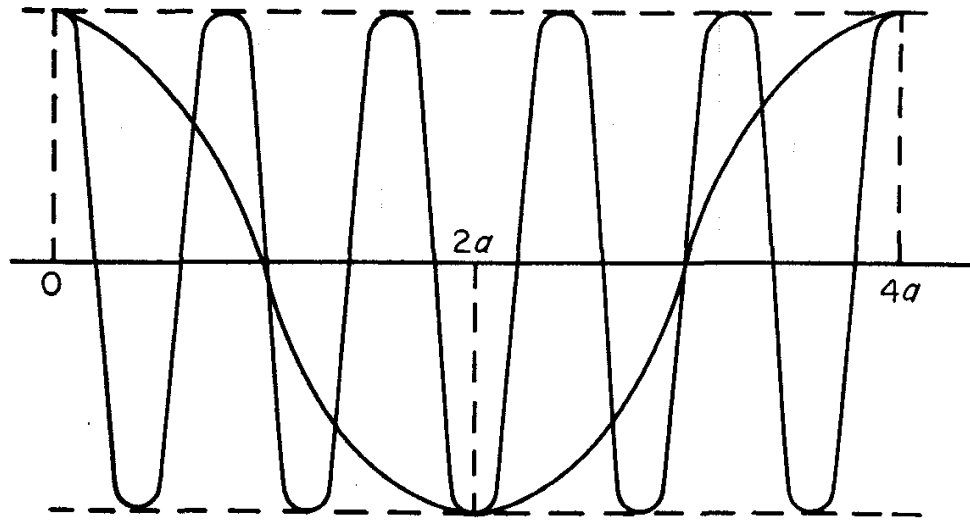
FIG. 4.3   Two equivalent lattice waves

Figure 4.3 illustrates the two equivalent cosine waves with $k' = \pi/2a$ and $k_1 = 5\pi/2a$. Both waves give the same atomic displacements. It is common practice to restrict k to lie within the range $-\pi/a \leqslant k \leqslant \pi/a$ and this region is called the Bril-

louin zone. (Brillouin zones will be discussed in detail in Chapter 5.) Also, for each ω, there are two values of k inside the Brillouin zone, which are equal in magnitude but opposite in sign. These correspond to waves moving in opposite directions. This degeneracy occurs also in two- and three-dimensional lattices.

At the 'maximum' frequency ω_m, the solution is a standing wave.

$$x_n = A e^{i\omega t} \cos n\pi \qquad (4.8)$$

There are in fact solutions corresponding to frequencies greater than ω_m but then k is complex and the waves are exponentially attenuated. For $\omega > \omega_m$ then $\left(\sin \dfrac{ka}{2}\right)^2 > 1$. The solutions are

$$k = \frac{\pi}{a} + i\beta \qquad \beta \text{ real}$$

with

$$\left(\cosh \frac{\beta a}{2}\right)^2 = \frac{\omega^2 m}{4\alpha} \qquad (4.9)$$

β is called the attenuation coefficient and increases rapidly with ω.
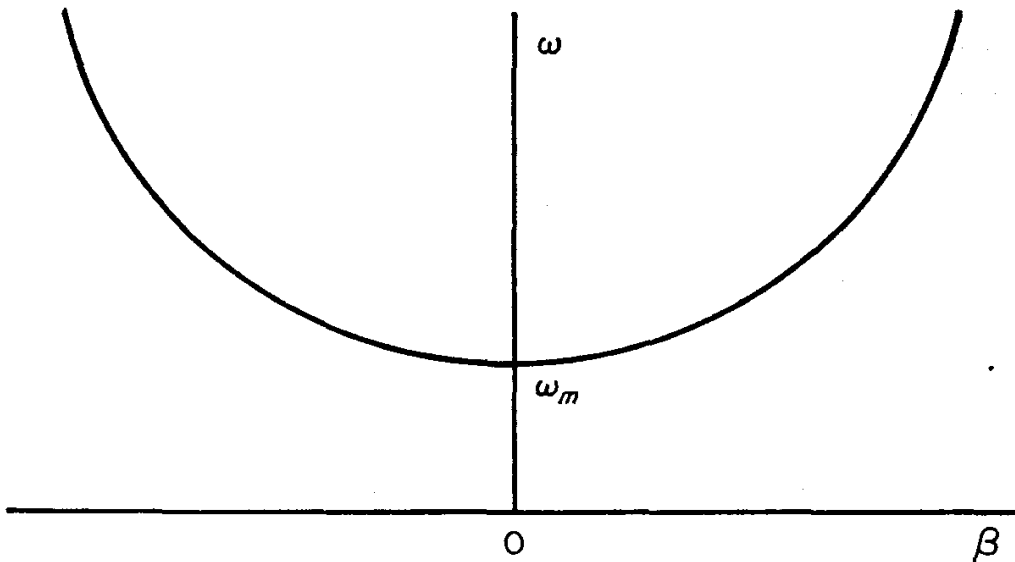
FIG. 4.4   Attenuation coefficient

The phase velocity of the waves is a function of k and

$$V = \frac{\omega}{k} = V_0 \frac{\sin (ka/2)}{(ka/2)} \qquad (4.10)$$

where $V_0 = \left(\dfrac{\alpha}{m}\right)^{\frac{1}{2}} a.$
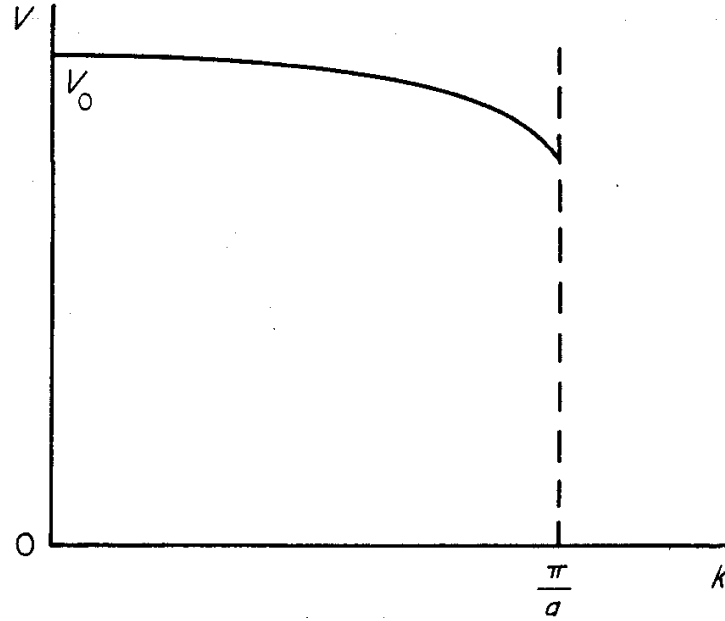
FIG. 4.5   Phase velocity

In the limit of long wavelengths (small k) the atomic description must be identical with the continuum treatment. From (4.10) the limiting value of the velocity as $k \longrightarrow 0$ is V_0. This should be compared with equation (4.1).

$$c^2 = \lambda/\rho$$

The modulus $\lambda = \alpha a$ and the average linear density $\rho = m/a$.

$$\therefore \qquad c^2 = \frac{\alpha a^2}{m} = V_0^2$$

as required.

In a crystal a reasonable value for the k giving the maximum frequency is $k = \pi/a \sim 10^8$ cm^{-1}. The wave velocity $\sim 10^5$ cm/sec and so the corresponding maximum frequency is $\sim 10^{13}$ rad/sec and lies in the infra-red region.

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Finite linear lattice

Consider a line of $N + 1$ atoms, the first and last atoms held fixed. For a frequency ω, the general solution of (4.4) is

$$x_n = e^{i\omega t}(Ae^{ikna} + Be^{-ikna}) \qquad (4.11)$$

A, B are arbitrary constants. The appropriate boundary conditions are

$$x_n = 0 \qquad n = 0 \qquad (a)$$
$$x_n = 0 \qquad n = N \qquad (b)$$

The first condition is satisfied if $A = -B$. The second condition requires

$$\sin(kNa) = 0$$

$$\therefore \qquad k = \frac{l\pi}{Na} \qquad l \text{ integer} \qquad (4.12)$$

The solutions are standing waves and

$$x_n = A'e^{i\omega t} \sin\left(n\frac{l\pi}{N}\right) \qquad (4.13)$$

It is clear from (4.13) that the negative values of l give the same solutions as the positive values and in fact there are $N - 1$ allowed standing waves corresponding to the $N - 1$ particles which are free to vibrate.

$$l = 1, 2, \ldots, (N - 1) \qquad (4.14)$$

Periodic boundary conditions

It is often more convenient to obtain travelling wave solutions. The infinite crystal is then assumed to be composed of identical microcrystals each containing N lattice points. The boundary conditions are

$$x_n = x_{n+N} \text{ for all } n \qquad (4.15)$$

A travelling wave of the type (4.5) satisfies this condition if

$$k = 2\frac{l\pi}{Na} \qquad l \text{ integer} \qquad (4.16)$$

The allowed values of k are spaced twice as far apart as those of (4.12). If the number of lattice points in the microcrystal is odd

$$l = \pm 1, \pm 2, \ldots, \pm \frac{(N-1)}{2} \qquad (4.17\ (a))$$

and if N is even

$$l = \pm 1, \pm 2, \ldots, \pm \frac{N}{2} \qquad (4.17\ (b))$$

In this latter case, the states with $l = \pm \frac{N}{2}$ are equivalent (4.7).

The total number of vibrations is $N - 1$ as before as now the positive and negative values of l correspond to independent states. Note that now in addition there is a non-zero solution with $l = 0$ (4.16) and that this corresponds to a translation of the crystal without change in potential energy and with zero frequency.

Frequency distribution

A frequency distribution $g(\omega)$ may be defined so that $g(\omega)d\omega$ is the number of allowed frequencies between ω and $\omega + d\omega$. The number of states in the element dk is $Nadk/\pi$ (4.12). (With periodic boundary conditions the number of states between $|k|$ and $|k + dk|$ is $2\left(\frac{Na}{2\pi}\right)dk = \frac{Na}{\pi}$ as before.)

$$g(\omega)\ d\omega = \frac{Na}{\pi} \frac{dk}{d\omega}\ d\omega$$

For a line of identical atoms (4.6)

$$k = \frac{2}{a}\sin^{-1}\left(\frac{\omega}{\omega_m}\right)$$

$$\therefore \quad \frac{dk}{d\omega} = \frac{2}{a(\omega_m{}^2 - \omega^2)^{\frac{1}{2}}}$$

$$\therefore \quad g(\omega) = \frac{2N}{\pi} \cdot \frac{1}{(\omega_m{}^2 - \omega^2)^{\frac{1}{2}}} \qquad (4.18)$$

This distribution function has a singularity when $\omega = \omega_m$ and the frequency modes are crowded near the cut-off frequency.
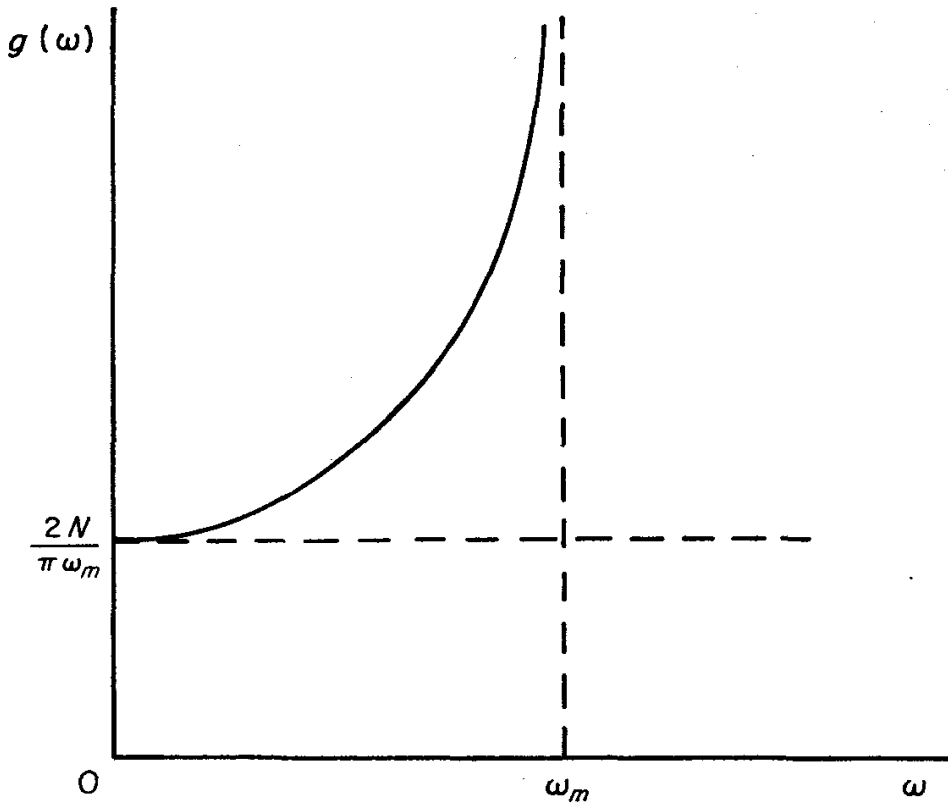
FIG. 4.6 Frequency distribution for the monatomic linear lattice

Interactions beyond nearest neighbours

The exclusion of interactions beyond the nearest neighbours is only a convenient approximation and a more accurate description is obtained if interactions over larger distances are considered. When the Mth neighbours are included the obvious generalization of (4.4) is

$$m\ddot{x}_n = \sum_{s=1}^{M} \alpha_s(x_{n+s} + x_{n-s} - 2x_n) \qquad (4.19)$$

The corresponding dispersion relation is

$$\omega^2 m = 2\sum_{s=1}^{M} \alpha_s(1 - \cos(ska)) \qquad (4.20)$$

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Once more ω^2 is periodic in k with period $2\pi/a$ and inside the Brillouin zone ω^2 is an even function and there is two-fold degeneracy (except at the origin). As cos (ska) may be expanded as a polynomial of degree s in cos ka the frequency may be expressed as a polynomial of degree M in cos ka. For a given frequency there are M solutions for cos ka and consequently M values for k in the range 0 to π/a. It is possible that some of these values are complex and correspond to damped solutions.
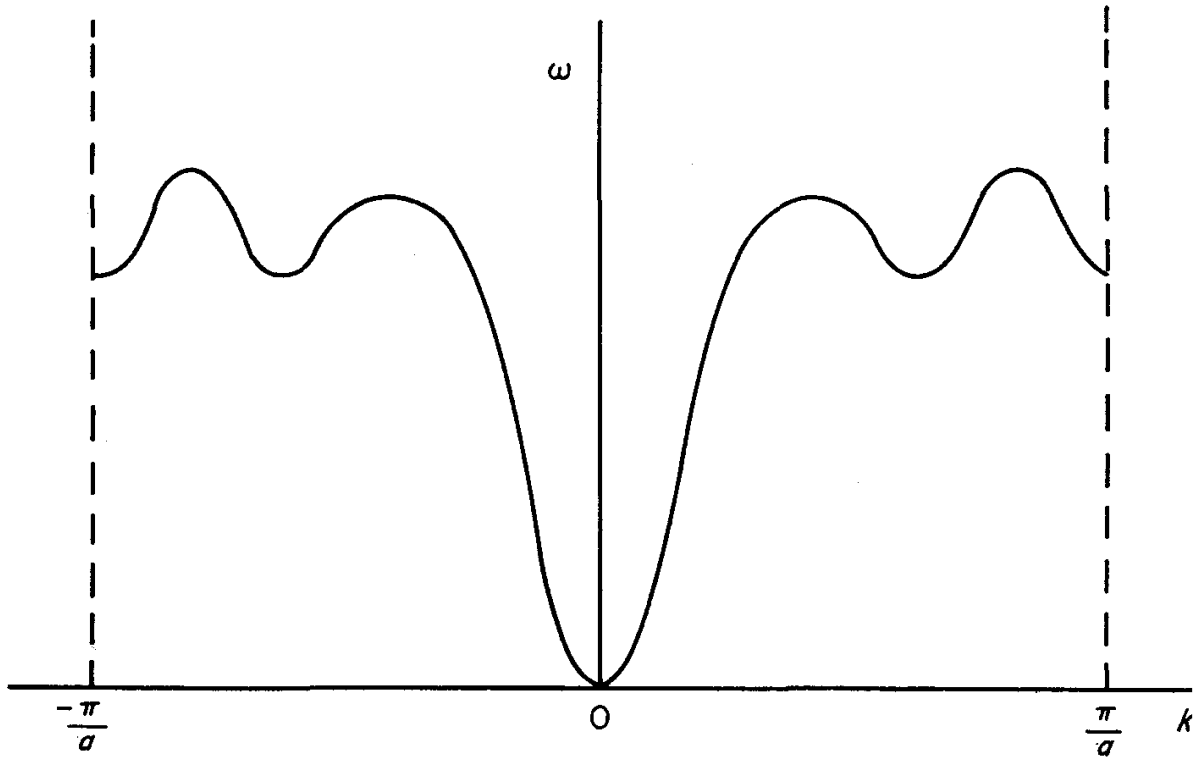
FIG. 4.7   Dispersion curve with many neighbour interactions

The maximum frequency does not necessarily occur at the points $\pm\pi/a$ although the dispersion curve must have a stationary value at these points.

Transverse waves

If the atoms can vibrate in a plane perpendicular to the line then transverse modes are possible. For small displacements it can readily be shown that the equations of motion are very similar to those for longitudinal motion (4.4). The lateral dis-

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placement y_n of the nth atom satisfies (nearest neighbour interaction only)

$$m\ddot{y}_n = \alpha'(y_{n+1} + y_{n-1} - 2y_n)$$

There is of course a new force constant α'. All the analysis of the previous sections will apply and for a linear lattice with cylindrical symmetry there will be two dispersion curves.
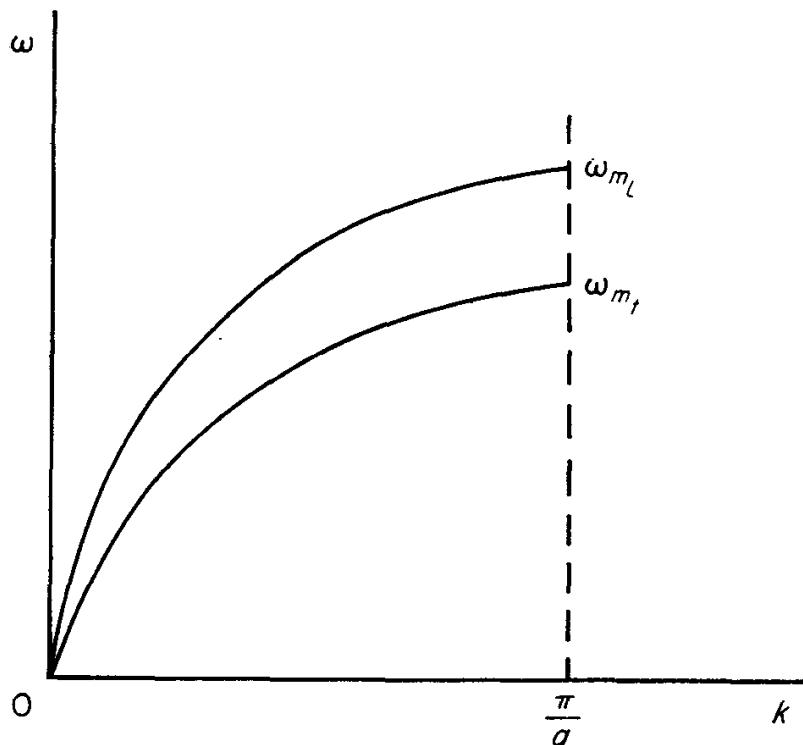
FIG. 4.8   Transverse and longitudinal waves

§ 4.3 A linear lattice with two types of atoms

Consider a line of atoms equally spaced at a distance a apart. Alternate atoms have masses M and m $(M > m)$. The primitive cell has a length $2a$ and contains two atoms.
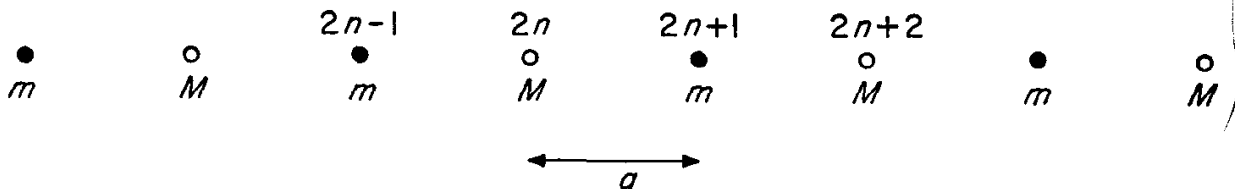
FIG. 4.9   Linear lattice with two types of atom

The masses M are located at the even sites $2n$ and the masses m at the odd sites $2n + 1$. When only nearest neighbour interactions are considered the equations of motion for the two types of atom are (longitudinal modes)

$$M\ddot{x}_{2n} = \alpha(x_{2n+1} + x_{2n-1} - 2x_n)$$

$$m\ddot{x}_{2n+1} = \alpha(x_{2n+2} + x_{2n} - 2x_{2n+1}) \qquad (4.21)$$

There exist travelling wave solutions of the type

$$x_{2n} = A_1 e^{i(\omega t + k2na)}, \quad x_{2n+1} = A_2 e^{i(\omega t + k\overline{2n+1}a)} \qquad (4.22)$$

The equations of motion are then

$$A_1(\omega^2 M - 2\alpha) + A_2 2\alpha \cos ka = 0$$

$$A_1 2\alpha \cos ka + A_2(\omega^2 m - 2\alpha) = 0 \qquad (4.23)$$

These two simultaneous equations have a non-trivial solution only if the determinant of coefficients is zero. This is a quadratic expression in ω^2 with

$$\omega^2 = \alpha\left(\frac{1}{M} + \frac{1}{m}\right) \pm \alpha\left[\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4 \sin^2 ka}{Mm}\right]^{\frac{1}{2}} \qquad (4.24)$$

The dispersion relation (4.24) is periodic in k with period π/a and the Brillouin zone is defined by $-\pi/2a \leqslant k \leqslant \pi/2a$. These two sets of solutions are known as the optical and acoustical branches. For long waves (small k), the two roots are

$$\omega_+^2 = 2\alpha\left(\frac{1}{M} + \frac{1}{m}\right) \qquad \text{optical}$$

$$\omega_-^2 = \frac{2\alpha}{M + m} \cdot k^2 a^2 \qquad \text{acoustical} \qquad (4.25)$$

For $k = \pm\pi/2a$, the two roots are

$$\omega_+^2 = \frac{2\alpha}{m} \qquad \text{optical}$$

$$\omega_-^2 = \frac{2\alpha}{M} \qquad \text{acoustical} \qquad (4.26)$$
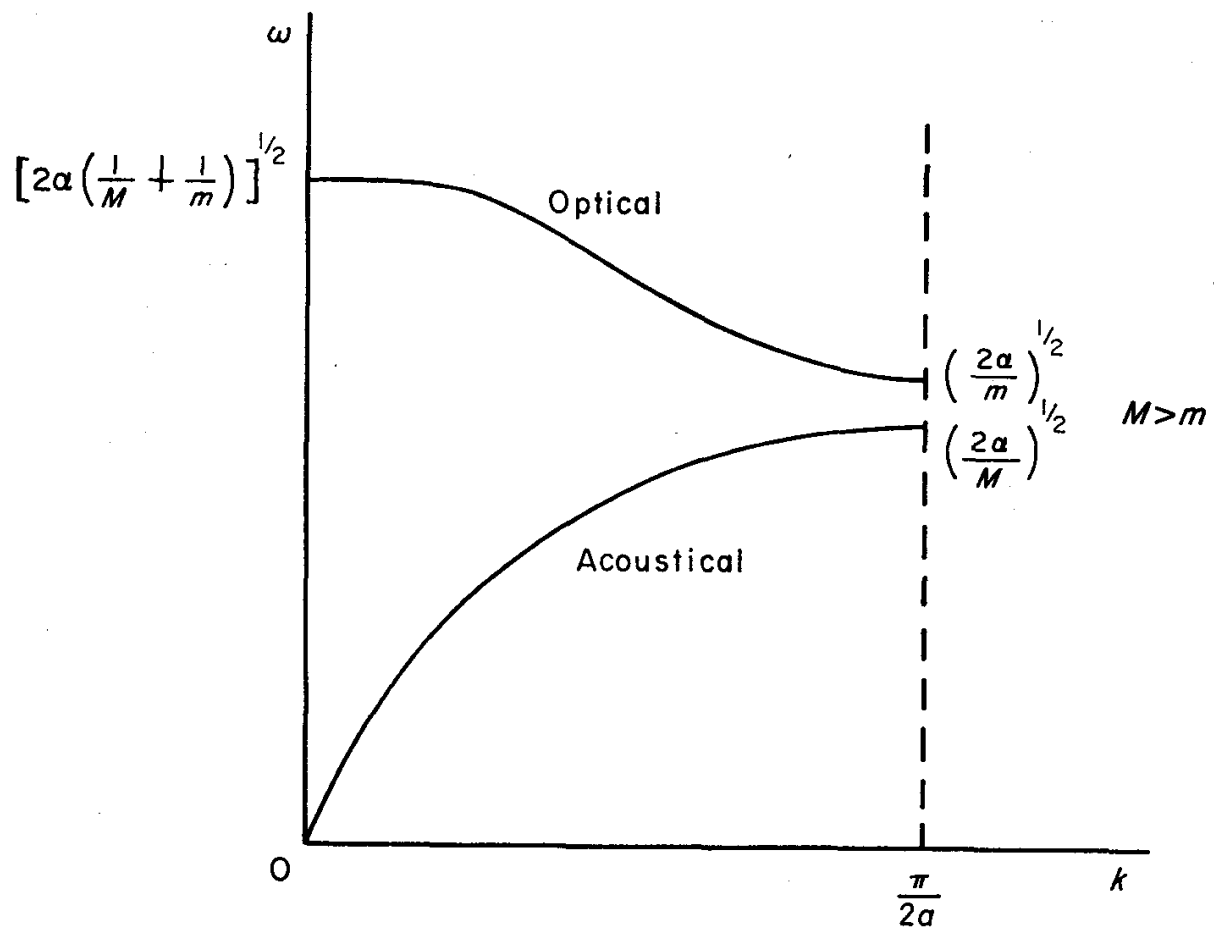
FIG. 4.10   Optical and acoustical branches
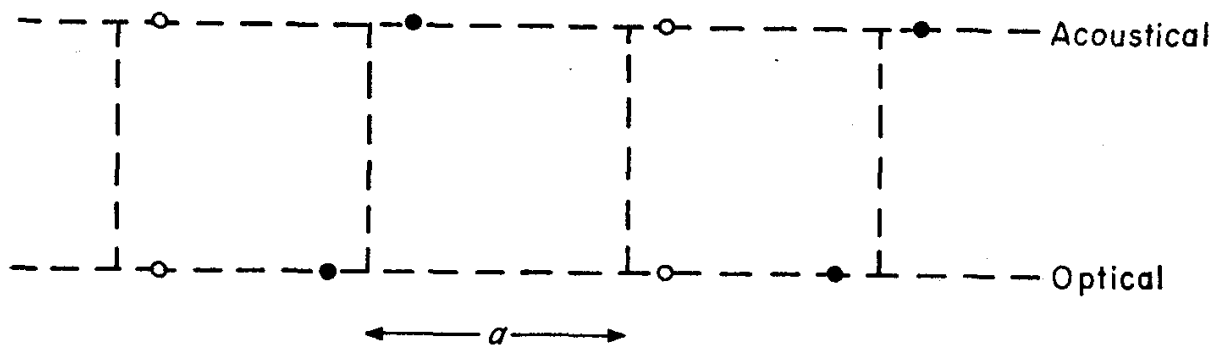
FIG. 4.11   Atomic motion for small k

From (4.23) and (4.25) it can be shown that in the limit of small k

$$\frac{A_1}{A_2} = 1 \qquad \text{acoustical branch}$$

$$\frac{A_1}{A_2} = -\frac{m}{M} \qquad \text{optical branch}$$

If the particles are ions with opposite charges then this latter type of motion may be excited by an electromagnetic wave. This maximum frequency represents the fundamental infra-red absorption frequency.

There is a frequency gap in the dispersion diagram (Fig. 4.10) in which k is complex and the waves are damped.

§ 4.4 Normal co-ordinates

Consider a crystal (or molecule) composed of N atoms. $3N$ position co-ordinates q_i are necessary to specify the positions of all the particles. If the interatomic forces are conservative a potential function V may be defined which depends upon the position co-ordinates. This potential has a minimum in the stable equilibrium configuration specified by $q_i = \alpha_i$ and all the first order derivatives are zero. If the system undergoes a small displacement from equilibrium so that $q_i = \alpha_i + \zeta_i$ then by Taylor's theorem to second order in ζ_i

$$V = \tfrac{1}{2}\left[\left(\zeta_1 \frac{\partial}{\partial q_1} + \ldots + \zeta_{3N} \frac{\partial}{\partial q_{3N}}\right)^2 V\right]_{\alpha_i} \qquad (4.27)$$

Here the zero of potential is the minimum. In this Harmonic approximation the potential energy is a quadratic function of the displacements. This corresponds to the Hooke law approximation in Sections 4.2 and 4.3 (see Problem 1).

$$V = \tfrac{1}{2}\sum_i^{3N} \sum_j f_{ij}\zeta_i\zeta_j$$

with $\qquad f_{ij} = f_{ji} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_{\alpha_i} = \text{constant} \qquad (4.28)$

The position co-ordinates may be chosen relative to a Cartesian set of axes and the kinetic energy is

$$T = \tfrac{1}{2} \sum_{i=1}^{3N} m_i \dot{\zeta}_i{}^2 \qquad \dot{\zeta}_i \equiv \frac{d\zeta}{dt} \qquad (4.29)$$

The normal co-ordinates Q_i are defined as the linear combinations of the co-ordinates ζ_i which bring the kinetic and potential energies simultaneously into the diagonal forms

$$T = \tfrac{1}{2} \sum_{1}^{3N} \dot{Q}_i{}^2 \qquad V = \tfrac{1}{2} \sum_{1}^{3N} \omega_i{}^2 Q_i{}^2 \qquad (4.30)$$

These co-ordinates can always be found and the process is briefly explained below. The kinetic energy (4.29) is easily dealt with by introducing 'mass-weighted' co-ordinates $\eta_i = \sqrt{m_i}\,\zeta_i$ and

$$T = \tfrac{1}{2} \sum_{i=1}^{3N} \dot{\eta}_i{}^2 \qquad V = \tfrac{1}{2} \sum_i \sum_j F_{ij} \eta_i \eta_j \qquad (4.31)$$

where
$$F_{ij} = f_{ij}/\sqrt{m_i \cdot m_j}$$

Any further orthogonal transformation will preserve the kinetic energy as a simple sum of squares. For example, define a new set of co-ordinates by an orthogonal transformation A_{ij}.

$$\eta_i = \sum_{j=1}^{3N} A_{ij} \theta_j \qquad (4.32)$$

In matrix formalism $\eta = A\theta$ where η, θ are column matrices. As A is orthogonal $A^{-1} = A'$ (A' is the transpose matrix) and so

$$\theta = A^{-1}\eta = A'\eta \qquad (4.33)$$

The kinetic energy term in (4.31) is

$$T = \tfrac{1}{2} \dot{\eta}'\dot{\eta} = \tfrac{1}{2}(A\dot{\theta})'(A\dot{\theta}) = \tfrac{1}{2}\dot{\theta}' A^{-1} A \dot{\theta} = \tfrac{1}{2}\dot{\theta}'\dot{\theta}$$

and the sum of squares is preserved by the orthogonal transformation. When the transformation is applied to the potential energy

$$V = \tfrac{1}{2}\eta' F\eta = \tfrac{1}{2}(A\theta)' F(A\theta) = \tfrac{1}{2}\theta'(A^{-1}FA)\theta$$

It can be shown that the orthogonal transformation can always be chosen so that $(A^{-1}FA)$ is a diagonal matrix with

$$(A^{-1}FA)_{ij} = \omega_i{}^2 \delta_{ij} \qquad (4.34)$$

(A complete discussion is given in Synge and Griffith's *Principles of Mechanics*.)

The co-ordinates θ_i are then the normal co-ordinates of (4.30).

The momentum P_i conjugate to Q_i is defined by $P_i = \dfrac{\partial T}{\partial \dot{Q}_i} = \dot{Q}_i$ and the Hamiltonian is

$$H = \tfrac{1}{2} \sum_{i=1}^{3N} P_i{}^2 + \tfrac{1}{2} \sum_{i=1}^{3N} \omega_i{}^2 Q_i{}^2 \qquad (4.35)$$

From Hamilton's equation $\dot{P}_i = -\dfrac{\partial H}{\partial Q_i}$

$$\ddot{Q}_i + \omega_i{}^2 Q_i = 0 \qquad i = 1, 2, \ldots, 3N \qquad (4.36)$$

For stable equilibrium V is positive definite and $\omega_i{}^2 > 0$ for all i. The solutions of (4.36) are

$$Q_i = Q_i{}^\circ \sin (\omega_i t + \epsilon_i) \qquad (4.37)$$

As the particle displacements are real the normal co-ordinates are real and vary harmonically in time with period $2\pi/\omega_i$. There are $3N$ such co-ordinates and frequencies corresponding to the $3N$ degrees of freedom of the system.

A general solution in terms of the co-ordinates η_i may be expressed as a linear combination of normal co-ordinates (4.32). The amplitudes and the phases of the normal co-ordinates are $6N$ constants chosen to fit the initial conditions of the system. If these are such that the $3N - 1$ normal co-ordinates Q_1, $Q_1, \ldots, Q_{r-1}, Q_{r+1}, \ldots, Q_{3N}$ are all permanently zero and $Q_r \neq 0$ then the system is vibrating in a normal mode. The motion of each particle is periodic with the same frequency ω_r and with the same phase. This is the type of solution obtained for the linear lattice in section 4.2 (equation (4.5)).

The allowed frequencies may be obtained from (4.34) or

from the equations below which are derived from (4.31) in the same way that (4.36) is obtained from (4.30).

$$\ddot{\eta}_i + \sum_j F_{ij}\eta_j = 0 \qquad i = 1, \ldots, 3N \qquad (4.38)$$

When the system is in the rth mode $\eta_i = A_{ir}Q_r$ and (4.38) becomes

$$\sum_j [F_{ij} - \omega_r^2\delta_{ij}]A_{jr} = 0 \qquad i = 1, \ldots, 3N \qquad (4.39)$$

For a non-trivial solution the determinant of coefficients is zero.

$$| F_{ij} - \omega_r^2\delta_{ij} | = 0 \qquad\qquad (4.40)$$

This is a polynomial of degree $3N$ in ω^2 and gives the $3N$ values for ω which are characteristic of the particle system. If two or more of the roots are coincident the system is said to be degenerate. For a given ω_r the equations (4.39) determine the relative values of the coefficients $A_{jr}, j = 1, 2, \ldots, 3N$. When this set is normalized it forms a column of the orthogonal transformation matrix.

It has been stated that V is positive definite and $\omega_r^2 > 0$ for all frequencies. This is not strictly true and in fact six frequencies are zero. (Five for a linear molecule.) These correspond to modes which represent a translation or rotation of the crystal. Clearly if each atom is given the same translation there is no change in potential energy and hence no restoring force. The system is in neutral equilibrium and V is semi-definite with respect to the six zero-frequency co-ordinates.

If the position of the centroid and orientation of the system are specified then there are $3N - 6$ 'internal' co-ordinates all with real, non-zero frequencies. For the longitudinal vibrations of a linear lattice (with periodic boundary conditions) there is only one zero frequency. However, if the ends of the crystal are fixed this translational mode is not allowed (4.14).

§ 4.5 Group theory and normal modes

A normal mode can be described by the $3N$ co-ordinates $\eta_i^\circ = A_{ir}Q_r^\circ$ giving the maximum displacements of the atoms from their equilibrium positions. The molecular symmetry may demand that several different modes possess the same frequency. For example consider an equilateral triangular molecule. Figure 4.12 (a) illustrates the atomic displacements for one of the normal modes. The distortion in 4.12 (b) is related by a mirror plane and so must represent a mode with the same frequency. It is in fact the same mode.

(a)   (b)
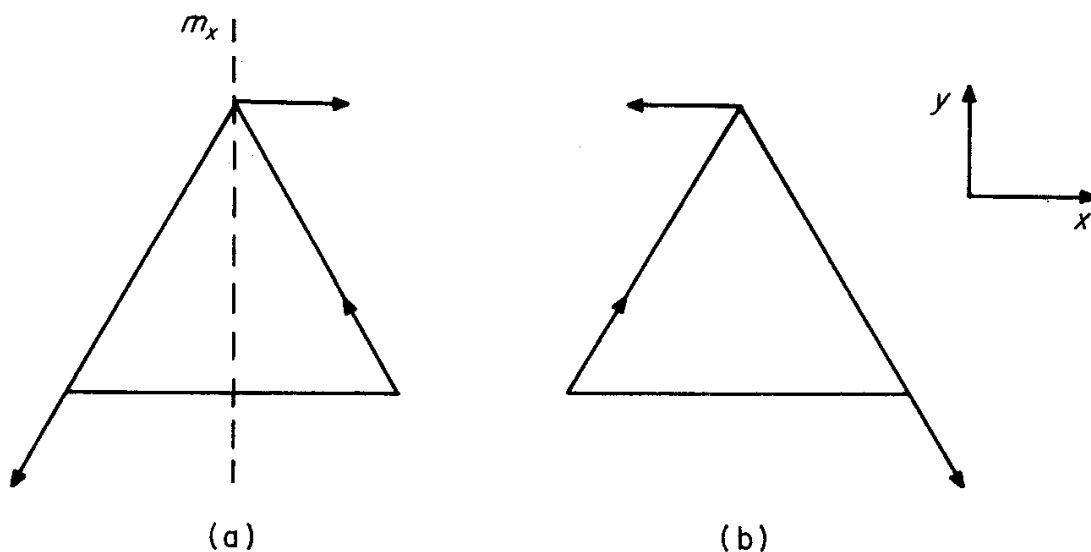
Fig. 4.12

For a non-degenerate frequency ω_i the normal co-ordinate must transform according to a real one-dimensional representation of the symmetry group of the molecule.

i.e. $$RQ_i = \pm Q_i$$

where R is any member of the group. For an n-fold degenerate frequency, the n normal co-ordinates $Q_1, \ldots, Q_n$ (say) must transform according to a real n-fold representation of the group.

$$RQ_i = \sum_{j=1}^{n} C_{ji}Q_i \qquad (4.41)$$

This representation will be irreducible apart from accidental degeneracies.

As an illustration consider the triangular 'molecule' of Fig. 4.12. If the two faces are not identical the symmetry group is $3m$ containing six elements. (It is suggested that the reader extend this treatment to the case of the ozone molecule with symmetry $\bar{6}m2$. See Section 3.6.) Table 4.1 is the character table.

TABLE 4.1

Character table for group $3m$

$3m$	E	$3z$	m_x
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0
χ_{tot}	9	0	1

Nine co-ordinates are necessary to specify the positions of all the atoms and so the representation of the group given by

Translational modes
E

Rotational mode
A_2
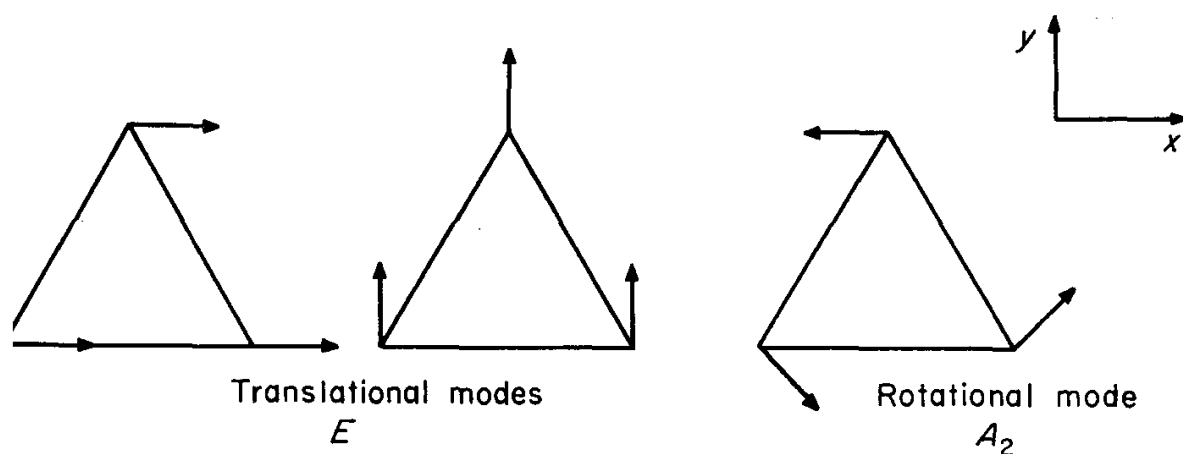
FIG. 4.13   Some zero-frequency modes

the normal co-ordinates is nine-dimensional. This 'total' representation is reducible. The characters of a representation are invariant under a change of basis functions (3.34) and so the

atomic displacements may conveniently be used to find the total representation. These characters are listed under χ_{tot} in Table 4.1. Note that for a given symmetry operation only those atoms which remain fixed can contribute to the character. By inspection the total representation is

$$2A_1 + A_2 + 3E$$

The translations account for representations $A_1 + E$ and the rotations for $A_2 + E$. These are the six zero frequency modes. The remaining three vibrational modes form a basis for the

A_1

Totally symmetric
mode

E
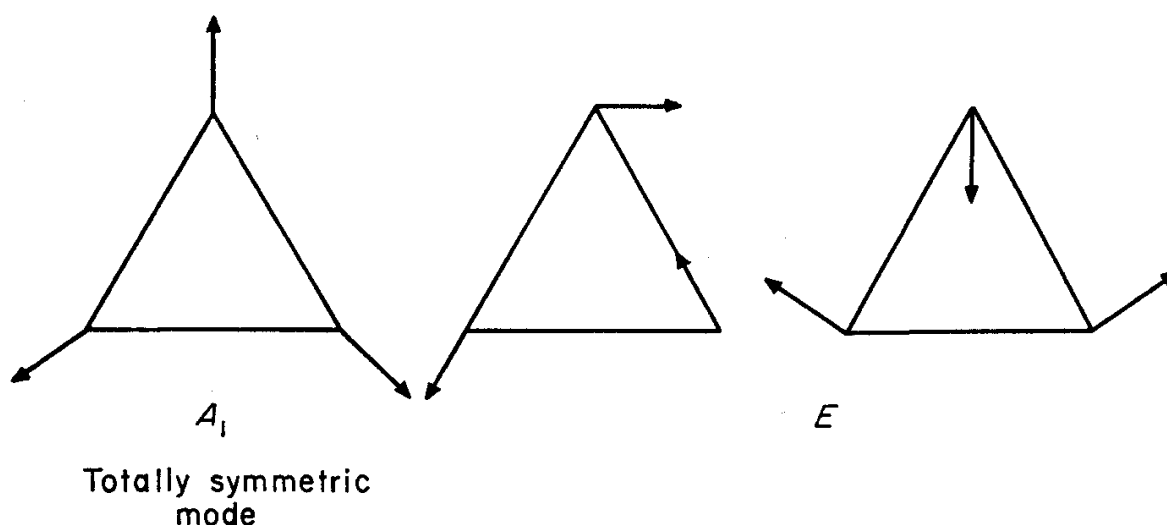
FIG. 4.14   Vibrational modes

representation $A_1 + E$. One of the vibrational modes is non-degenerate while the other two form a degenerate pair (Fig. 4.14).

§ 4.6 Normal modes and the linear lattice

The vibrations of the linear lattice have been discussed in some detail in Sections 4.2 and 4.3, but it is instructive to relate the results obtained with the theory of normal modes.

Consider an infinite line of identical atoms distance a apart. Using periodic boundary conditions, the lattice is assumed to be

composed of microcrystals containing N atoms. The N normal frequencies are given by (4.6) (or more generally by (4.20)) with

$$k = \frac{2\pi}{Na}l \qquad l = 0, \pm 1, \ldots, \pm\frac{N-1}{2} \qquad N \text{ odd}$$

$l = 0$ gives the zero-frequency translational mode. Each of the normal co-ordinates must be real so that the atomic displacements are real when the system is vibrating in a normal mode. However, it is customary to introduce complex co-ordinates R_k defined by

$$R_k = \frac{1}{\sqrt{N}}\sum_{n=0}^{N-1}e^{-ikna}x_n \quad \text{or} \quad R_l = \frac{1}{\sqrt{N}}\sum_{n=0}^{N-1}e^{-i\frac{2\pi}{N}ln}x_n \quad (4.42)$$

Conversely, from the result

$$\sum_{l=-\frac{N-1}{2}}^{\frac{N-1}{2}} e^{i\frac{2\pi}{N}l(n-n')} = N\delta_{nn'} \qquad (4.43)$$

$$x_n = \frac{1}{\sqrt{N}} \sum_{l=-\frac{N-1}{2}}^{\frac{N-1}{2}} e^{+i\frac{2\pi}{N}ln}R_l \qquad (4.44)$$

(Compare (4.32) and (4.33).)

On substitution of (4.44) into equation (4.4) (or (4.19)) it is easily verified that

$$\ddot{R}_l + \omega_l^2 R_l = 0 \qquad (4.45)$$

Compare this with equation (4.36). The general solution for R_l is

$$R_l = A_l^- e^{-i\omega t} + A_l^+ e^{i\omega t} \qquad \omega > 0 \qquad (4.46)$$

A necessary condition to ensure the reality of the atomic displacements is $R_l = R^*_{-l}$ so that the complex co-ordinates are not completely independent. The correct number of independent normal co-ordinates is obtained by taking the real and imaginary parts. The kinetic and potential energies of the linear lattice are

$$T = \frac{m}{2}\sum_{n=0}^{N-1}\dot{x}_n^2 \qquad V = \frac{\alpha}{2}\sum_{n=0}^{N-1}(x_n - x_{n+1})^2 \qquad (4.47)$$

V is correct for first neighbour interactions only. It is left as an exercise for the reader to confirm that

$$T = \frac{m}{2} \sum_{l=-\frac{N-1}{2}}^{\frac{N-1}{2}} \dot{R}_l{}^*\dot{R}_l \qquad V = \frac{m}{2} \sum_{l=-\frac{N-1}{2}}^{\frac{N-1}{2}} \omega_l{}^2 R_l{}^*R_l \quad (4.48)$$

These equations remain true when further neighbour interactions are included. (Compare (4.30). The present co-ordinates are not mass-weighted.)

The linear lattice is invariant under the group of N translations $\{\epsilon \mid ma\}$. This group is Abelian and the N irreducible representations are one-dimensional. The complex co-ordinates are each a basis for one of these irreducible representations. As the co-ordinates are complex there is now no need to demand real representations. The operator $\{\epsilon \mid ma\}$ is defined so that

$$\{\epsilon \mid ma\}x_n = x_{n-m}$$

and by operating on (4.42)

$$\{\epsilon \mid ma\}R_l = e^{-i_N{}^{lm}}R_l$$

i.e. $$\{\epsilon \mid ma\}R_k = e^{-ikma}R_k$$

The irreducible representations may be labelled by the wave vector so that in the kth representation $\{\epsilon \mid ma\}$ is represented by e^{-ikma}. The representations of the translation group will be considered in more detail with reference to the Bloch theorem in Chapter 5.

§ 4.7 Quantum theory of lattice vibrations

Up to this point the treatment of lattice vibrations has been classical. Certainly the wave vector takes discrete values so that the frequency band is quasi-continuous but this is not a quantum effect. However, it is a relatively simple task to reformulate the problem in quantum terms. The quantum energy levels are necessary to give the theory of specific heat.

It has been shown that for a linear crystal the total energy is

$$E = \frac{m}{2} \sum_{l=-\frac{N-1}{2}}^{\frac{N-1}{2}} (\dot{R}_l^* \dot{R}_l + \omega_l^2 R_l^* R_l) \qquad (4.49)$$

N real normal co-ordinates are defined by

$$Q_{1l} = \frac{1}{\sqrt{2}}(R_l^* + R_l) \quad Q_{2l} = \frac{i}{\sqrt{2}}(R_l^* - R_l) \quad (4.50)$$

and the total vibrational energy of the lattice is

$$E = \frac{m}{2} \sum_{l=1}^{\frac{N-1}{2}} \sum_{i=1}^{2} (\dot{Q}^2_{il} + \omega_l^2 Q^2_{il}) \qquad (4.51)$$

Note that the sum is over the positive half of the Brillouin zone excluding the origin. The single $l = 0$ mode gives the translational energy. It is not difficult to show that the new independent co-ordinates represent standing wave modes. From (4.44) and (4.50) the atomic displacements due to the single co-ordinate Q_{1l} are

$$x_n = \sqrt{\frac{2}{N}} \cos\left(\frac{2\pi}{N}ln\right) Q^\circ_{1l} \sin(\omega_l t + \epsilon_l) \qquad (4.52)$$

The momentum conjugate to Q_{il} is $P_{il} = \dfrac{\partial T}{\partial \dot{Q}_{il}} = m\dot{Q}_{il}$ and the classical Hamiltonian is

$$H = \sum_{l=1}^{\frac{N-1}{2}} \sum_{i=1}^{2} \left[\frac{P^2_{il}}{2m} + \frac{m}{2}\omega_l^2 Q^2_{il}\right] \qquad (4.53)$$

The Schrödinger Hamiltonian corresponding to (4.53) is

$$\mathscr{H} = \sum_{l=1}^{} \sum_{i=1}^{} \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial Q_{il}^2} + \frac{m}{2}\omega_l^2 Q^2_{il}\right] \qquad (4.54)$$

This Schrödinger equation is separable in the normal co-ordinates and the many particle wave function is the product of $(N-1)$ single particle wave functions satisfying

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial Q_{il}^2} + \frac{m}{2}\omega_l^2 Q^2_{il}\right]\psi_{il} = E\psi_{il} \qquad (4.55)$$

That is, in the harmonic approximation the crystal may be treated as $N - 1$ independent harmonic oscillators with frequencies given by the classical dispersion relation (4.6) (or (4.20)). It is well known that the solutions of (4.55) are the Hermite functions and the single particle energies are

$$E_{tl} = (n_{tl} + \tfrac{1}{2})\hbar\omega_l \qquad (4.56)$$

where n_{tl} is a positive integer or zero. The total energy of the lattice vibrations is obtained by summing (4.56) over the $N - 1$ vibrational modes and the lowest allowed energy is $\sum\limits_{l>0} \hbar\omega_l$. This is called the zero-point energy and is an expression of the uncertainty principle.

It is possible to transform to real normal co-ordinates which represent running waves, but to do this it is necessary to use a contact transformation which mixes R_l and $\dot{R}_l$. The new co-ordinates are defined by

$$Q_l = \tfrac{1}{2}\left[(R_l + R_l^*) + \frac{i}{\omega_l}(\dot{R}_l - \dot{R}_l^*)\right] \qquad (4.57)$$

Conversely

$$R_l = \tfrac{1}{2}\left[(Q_l + Q_{-l}) + \frac{i}{\omega_l}(\dot{Q}_l - \dot{Q}_{-l})\right] \qquad (4.58)$$

Clearly Q_l satisfies equation (4.36) (see 4.45) and is given by (4.37). From (4.44) and (4.58) the displacements due to the single co-ordinate Q_l are

$$x_n = \frac{Q_l^\circ}{\sqrt{N}} \sin\left(-\frac{2\pi}{N}ln + \omega_l t + \epsilon_l\right) \qquad (4.59)$$

In terms of these normal co-ordinates the classical Hamiltonian is

$$H = \sum_{l=-\frac{N-1}{2}}^{\frac{N-1}{2}} \left[\frac{P_l^2}{2m} + \frac{m}{2}\omega_l^2 Q_l^2\right] \quad \text{with} \quad P_l = m\dot{Q}_l \qquad (4.60)$$

The quantum mechanical Hamiltonian is again separable in the normal co-ordinates and the many-particle wave function

is the product of $N - 1$ Hermite functions. (The $l = 0$ mode is omitted). Once more the modes are divided into degenerate pairs and the allowed lattice energies are the same as before.

There is an interesting alternative quantum description of the lattice vibrations. Regarding the real running-wave normal co-ordinates as Schrödinger operators, new operators may be defined by

$$a_l = \sqrt{\frac{\omega_l m}{2\hbar}} Q_l + i \sqrt{\frac{1}{2\hbar\omega_l m}} P_l \qquad (4.61)$$

$$a_l^+ = \sqrt{\frac{\omega_l m}{2\hbar}} Q_l - i \sqrt{\frac{1}{2\hbar\omega_l m}} P_l$$

a_l^+ is the Hermitian conjugate of the operator a_l (See Landau and Liftshitz *Quantum Mechanics*). Equations (4.61) may be inverted to give

$$Q_l = \sqrt{\frac{\hbar}{2\omega_l m}}(a_l^+ + a_l) \quad P_l = i\sqrt{\frac{\hbar\omega_l m}{2}}(a_l^+ - a_l) \quad (4.62)$$

The quantum mechanical Hamiltonian for a single mode is then

$$H_l = \frac{\hbar\omega_l}{2}(a_l^+ a_l + a_l a_l^+) \qquad (4.63)$$

With the infinite set of Hermite function solutions of the travelling-wave oscillator as basis the operators may be represented by matrices. Obviously the Hamiltonian is represented by the diagonal matrix.

$$[H_l] = \hbar w_l \begin{bmatrix} \frac{1}{2} & 0 & 0 \dots \\ 0 & \frac{3}{2} & 0 \\ 0 & 0 & \frac{5}{2} \\ \vdots & & \\ 0 & \dots \dots \end{bmatrix} \qquad (4.64)$$

The eigenfunction with energy $(n_l + \frac{1}{2})\hbar\omega_l$ is represented by a column matrix

momentum' requires further discussion. This is referred to again in Chapter 6.

The higher non-harmonic terms in the Taylor expansion (4.27) produce interactions between the phonons, and the phonon has a finite lifetime (van Hove, 1959; Peierls, 1929).

§ 4.8 Three-dimensional lattices

Apart from the general discussion of normal modes (Section 4.4) the above theory is concerned with linear lattices. No attempt is made in this text to give the complete three-dimensional theory but some important results are indicated below. In analogy to 4.5 there are solutions in which the atoms vibrate with the same frequency.

$$x_{in} = A_{in}e^{i(\omega t + k.R_n)} \tag{4.73}$$

x_{in} is the displacement in the ith direction of the atom at $R_n = n_1a_1 + n_2a_2 + n_3a_3$. The crystal is assumed to be composed of identical microcrystals with edges Na_1, Na_2, Na_3. These periodic boundary conditions require

$$N(k . a_i) = l_i 2\pi \qquad l_i \text{ integer}$$

For simplicity the lattice basis vectors will be assumed orthogonal and the components of the wave vector are

$$k_i = l_i \frac{2\pi}{Na_i} \tag{4.74}$$

There are N^3 distinct k-values and these may be chosen so that

$$-\frac{(N-1)}{2} \leqslant l_i \leqslant \frac{N-1}{2} \qquad N \text{ odd} \tag{4.75}$$

These values of k lie within a rectangular parallelepiped with corners at

$$k = \tfrac{1}{2}[\pm b_1 \pm b_2 \pm b_3] \tag{4.76}$$

where the vector b_i is parallel to a_i and $b_i = 2\pi/a_i$. This

is the product of $N - 1$ Hermite functions. (The $l = 0$ mode is omitted). Once more the modes are divided into degenerate pairs and the allowed lattice energies are the same as before.

There is an interesting alternative quantum description of the lattice vibrations. Regarding the real running-wave normal co-ordinates as Schrödinger operators, new operators may be defined by

$$a_l = \sqrt{\frac{\omega_l m}{2\hbar}} Q_l + i\sqrt{\frac{1}{2\hbar\omega_l m}} P_l \qquad (4.61)$$

$$a_l^+ = \sqrt{\frac{\omega_l m}{2\hbar}} Q_l - i\sqrt{\frac{1}{2\hbar\omega_l m}} P_l$$

a_l^+ is the Hermitian conjugate of the operator a_l (See Landau and Liftshitz *Quantum Mechanics*). Equations (4.61) may be inverted to give

$$Q_l = \sqrt{\frac{\hbar}{2\omega_l m}}(a_l^+ + a_l) \quad P_l = i\sqrt{\frac{\hbar\omega_l m}{2}}(a_l^+ - a_l) \quad (4.62)$$

The quantum mechanical Hamiltonian for a single mode is then

$$H_l = \frac{\hbar\omega_l}{2}(a_l^+ a_l + a_l a_l^+) \qquad (4.63)$$

With the infinite set of Hermite function solutions of the travelling-wave oscillator as basis the operators may be represented by matrices. Obviously the Hamiltonian is represented by the diagonal matrix.

$$[H_l] = \hbar\omega_l \begin{bmatrix} \frac{1}{2} & 0 & 0 \dots \\ 0 & \frac{3}{2} & 0 \\ 0 & 0 & \frac{5}{2} \\ \vdots & & \\ 0 & \dots \dots \end{bmatrix} \qquad (4.64)$$

The eigenfunction with energy $(n_l + \frac{1}{2})\hbar\omega_l$ is represented by a column matrix

$$| n_l > = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{bmatrix} \begin{matrix} 0 \\ 1 \\ \\ n_l - 1 \\ n_l \\ n_l + 1 \end{matrix} \qquad (4.65)$$

The matrices representing Q_l and P_l are Hermitian and (see Sneddon's book *Special Functions of Mathematical Physics and Chemistry* for properties of Hermite functions)

$$Q_l = \sqrt{\frac{\hbar}{2\omega_l m}} \begin{bmatrix} 0 & \sqrt{1} & 0 & 0 & 0 \dots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 & \sqrt{3} & 0 \\ \vdots & & & & \end{bmatrix}$$

$$P_l = i\sqrt{\frac{\hbar\omega_l m}{2}} \begin{bmatrix} 0 & -\sqrt{1} & 0 & 0 \dots \\ \sqrt{1} & 0 & -\sqrt{2} & 0 \\ 0 & \sqrt{2} & 0 & -\sqrt{2} \\ \vdots & & & \end{bmatrix} \qquad (4.66)$$

Then

$$a_l = \begin{bmatrix} 0 & \sqrt{1} & 0 & 0 \dots \\ 0 & 0 & \sqrt{2} & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ \vdots & & & \end{bmatrix}$$

$$a_l^+ = \begin{bmatrix} 0 & 0 & 0 \dots \\ \sqrt{1} & 0 & 0 \\ 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{3} \\ \vdots & & \end{bmatrix} \qquad (4.67)$$

Observe that a_l and a_l^+ are not Hermitian. By matrix multiplication

$$a_l^+ a_l = \begin{bmatrix} 0 & 0 & 0 & 0 \dots \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \\ \vdots & & & \\ \vdots & & & \end{bmatrix}$$

(4.68)

and $a_l a_l^+ - a_l^+ a_l = 1$. The Hamiltonian (4.63) becomes

$$H_l = \hbar\omega_l(na_l^+ a_l + \tfrac{1}{2})$$

(4.69)

in agreement with (4.64). The operators a_l and a_l^+ have the property

$$a_l \mid n_l > = \sqrt{n_l} \mid n_l - 1 > \quad a_l^+ \mid n_l > = \sqrt{n_l + 1} \mid n_l + 1 >$$

(4.70)

and so may be regarded as quantum annihilation and creation operators, respectively.

The many-particle state is completely described by the list of quantum numbers n_l and the state function may be written $\mid n_1 \dots n_{N-1} >$ with

$$a_l^+ a_l \mid n_1 \dots n_{N-1} > = n_l \mid n_1 \dots n_{N-1} >$$

(4.71)

$$n_l = 0, 1, 2, \dots$$

The total Hamiltonian is obtained by summing (4.63) over l (exclude $l = 0$) and the eigenvalues of the vibrational energy are

$$E = \sum_l \hbar\omega_l(n_l + \tfrac{1}{2})$$

(4.72)

The state is defined by the number of quanta of excitation in each running wave mode. These quanta may be regarded as particles and are called phonons. (Compare the theory of photons.) There can be any number of quanta in each mode and the phonons obey Bose–Einstein statistics.

In essence, the crystal lattice is replaced by a non-interacting gas of phonons with energies $\hbar\omega_l$. It can be shown that in collisions with electrons the quantity $\hbar k_l$ manifests itself as a type of linear momentum. As k is not uniquely determined for a lattice mode (4.7) the strict interpretation of the 'phonon

momentum' requires further discussion. This is referred to again in Chapter 6.

The higher non-harmonic terms in the Taylor expansion (4.27) produce interactions between the phonons, and the phonon has a finite lifetime (van Hove, 1959; Peierls, 1929).

§ 4.8 Three-dimensional lattices

Apart from the general discussion of normal modes (Section 4.4) the above theory is concerned with linear lattices. No attempt is made in this text to give the complete three-dimensional theory but some important results are indicated below. In analogy to 4.5 there are solutions in which the atoms vibrate with the same frequency.

$$x_{in} = A_{in}e^{i(\omega t + k.R_n)} \tag{4.73}$$

x_{in} is the displacement in the ith direction of the atom at $R_n = n_1 a_1 + n_2 a_2 + n_3 a_3$. The crystal is assumed to be composed of identical microcrystals with edges $N a_1$, $N a_2$, $N a_3$. These periodic boundary conditions require

$$N(k . a_i) = l_i 2\pi \qquad l_i \text{ integer}$$

For simplicity the lattice basis vectors will be assumed orthogonal and the components of the wave vector are

$$k_i = l_i \frac{2\pi}{N a_i} \tag{4.74}$$

There are N^3 distinct k-values and these may be chosen so that

$$-\frac{(N-1)}{2} \leqslant l_i \leqslant \frac{N-1}{2} \qquad N \text{ odd} \tag{4.75}$$

These values of k lie within a rectangular parallelepiped with corners at

$$k = \tfrac{1}{2}[\pm b_1 \pm b_2 \pm b_3] \tag{4.76}$$

where the vector b_i is parallel to a_i and $b_i = 2\pi/a_i$. This

FIG. 4.15   Section through the Brillouin zone when $r = 2$

volume is called the Brillouin zone. (See Chapter 5 for a more complete discussion.) When there is one atom per primitive cell substitution of (4.73) in the three-dimensional analogue of 4.4 results in a cubic expression for ω^2 and each root is a continuous function of k, periodic in the Brillouin zone. For a given value of the wave vector there are three frequencies all of which go to zero as $k \longrightarrow 0$. These are the three acoustical branches. Note that there are $3N^3$ normal modes as expected. At 'symmetry' points in the Brillouin zone there may be degeneracies between the different branches and it may be possible to distinguish a longitudinal mode and two transverse modes. However, for a general wave vector there is no degeneracy and there is no definite distinction between longitudinal and transverse modes. For each branch of the spectrum $\omega^2(k) = \omega^2(-k)$.

If there is a basis of r atoms per cell there will be $3r$ modes for each k. The additional modes are called optical modes and do not go to zero as $k = 0$.

The quantization of the vibrational modes follows as in the previous section and the crystal may again be regarded as a system of independent quantum oscillators.

Information about the lattice spectrum has been found experimentally by the scattering of X-rays and thermal neutrons. The neutron method is most appropriate as the energy of the thermal neutrons is of the same order as the lattice waves.

§ 4.9 The lattice specific heat

Classical theory

It is well known that classical theory predicts that the heat capacity at constant volume is independent of temperature. In the harmonic approximation, the vibrations of a crystal composed of N^3 identical atoms can be described in terms of $3N^3$ normal co-ordinates each with a characteristic frequency. (Strictly six of these frequencies are zero.) From classical

statistical mechanics it is simple to show that the mean energy of an oscillator in thermal equilibrium is kT where T is the absolute temperature. The total internal energy of the crystal is

$$U = 3N^3 kT \tag{4.77}$$

(Here k is the Boltzmann constant. Later it will be used also for the wave vector). For one mole, $N^3 = 6 \cdot 025 \cdot 10^{23}$ (Avagadro's number) and

$$U = 3RT \tag{4.78}$$

where R is the gas constant. The lattice contribution to the molar heat capacity at constant volume is

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3R \sim 6 \text{ cal/deg mole} \tag{4.79}$$

So classical theory predicts that the heat capacity per mole is the same for all substances at all temperatures. At room temperature and above many materials obey this law, but the agreement fails at lower temperatures. Experimentally it is found that the heat capacity approaches zero as $T \longrightarrow 0$. Near absolute zero the heat capacity of metals decreases as T. This is due to the conduction electrons and was mentioned in Chapter 2. For non-metals the heat capacity approaches zero as T^3. This effect is characteristic of the lattice vibrations.

Quantum theory

In Section 4.7 it was explained how the normal mode oscillators are quantized with energy levels

$$E_l = (n_l + \tfrac{1}{2})\hbar\omega_l$$

There is no restriction upon the number of phonons in a given mode and they obey Bose–Einstein statistics. On average the number of phonons in the mode with angular frequency ω at the temperature T is

$$\bar{n}(\omega) = 1/(e^{\hbar\omega/kT} - 1) \tag{4.80}$$

The mean energy of the normal mode is

$$\bar{E}(\omega) = [\bar{n}(\omega) + \tfrac{1}{2}]\hbar\omega \tag{4.81}$$

The total internal energy is obtained by summing over all modes. As the frequencies lie close together it is convenient to replace the sum by an integral. A frequency distribution is defined so that $g(\omega)\,d\omega$ is the number of allowed frequencies between ω and $\omega + d\omega$. This function must satisfy

$$\int g(\omega)\,d\omega = 3N^3 \qquad (4.82)$$

$g(\omega)$ is a sum of contributions from the different branches of the vibration spectrum. The total internal energy is

$$U = \int g(\omega)\bar{E}(\omega)\,d\omega \qquad (4.83)$$

The difficulty arises in the derivation of $g(\omega)$.

Einstein considered the simplest possible model (1907, 1911). He assumed that all the modes have the same frequency ω_0. The internal energy is then

$$U = 3N^3\bar{E}(\omega_0)$$

$$= 3N^3\left[\frac{1}{e^{\hbar\omega_0/kT} - 1} + \tfrac{1}{2}\right]\hbar\omega_0 \qquad (4.84)$$

The heat capacity at constant volume is

$$C_v = \frac{\partial U}{\partial T} = 3N^3k\left(\frac{\theta_E}{T}\right)^2\frac{e^{\theta_E/T}}{[e^{\theta_E/T} - 1]^2} \qquad (4.85)$$

where the Einstein temperature θ_E is defined by $\hbar\omega_0 = k\theta_E$. θ_E for a material is chosen to make equation (4.85) give a reasonable fit to the experimental results and typically is of the order of a few hundred degrees absolute. Einstein's formula is in fair agreement with experiment for $T >> \theta_E$ but at low temperatures when $T << \theta_E$ the agreement is poor. Instead of giving a T^3 variation

$$C_v = 3N^3k\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T} \qquad T << \theta_E \qquad (4.86)$$

To obtain the heat capacity at very low temperature it is only necessary to know $g(\omega)$ for small frequencies as the mean

energy $\bar{E}(\omega)$ becomes small when ω is large. The motions of adjacent atoms are certainly not independent for these important long wavelength modes. The Debye model (1912) successfully explains the T^3 variation at low temperatures. In the Debye theory the acoustical spectrum of a solid is treated as if the material is homogeneous and all the lattice waves travel with the same phase velocity; the ordinary velocity of sound. This is clearly reasonable for very small frequencies and these are the important modes at low temperatures. For a diatomic solid, the Einstein model may be used for the optical branches.

A cut-off frequency is defined so that the total number of acoustical frequencies is $3N^3$. The number of modes in a given branch of the spectrum with wave vector less than k is (from 4.74)

$$M(k) = \frac{4}{3}\pi k^3 \Big/ \frac{(2\pi)^3}{\Omega} \qquad (4.87)$$

where Ω is the crystal volume. So the number of modes with wave vector between k and $k + \mathrm{d}k$ is

$$N(k)\,\mathrm{d}k = \frac{k^2}{2\pi^2}\mathrm{d}k\Omega \qquad (4.88)$$

and the number of modes with frequency between ω and $\omega + \mathrm{d}\omega$ is

$$g(\omega)\,d\omega = N(k)\frac{\mathrm{d}k}{\mathrm{d}\omega}\mathrm{d}\omega \qquad (4.89)$$

$\dfrac{\mathrm{d}k}{\mathrm{d}\omega}$ depends upon the form of the frequency spectrum. Debye took

$$k = \frac{\omega}{C} \quad \text{i.e.} \quad \frac{\mathrm{d}k}{\mathrm{d}\omega} = \frac{1}{C} \qquad (4.90)$$

where C is a constant velocity and so

$$g(\omega) = \frac{\omega^2\Omega}{2\pi^2 C^3}. \qquad (4.91)$$

For a three-dimensional crystal there are three acoustical branches. If it is assumed that the medium is isotropic (no

crystal is) so that the spectrum can be described by one longitudinal and two degenerate transverse branches with phase velocities C_l and C_t respectively then

$$g(\omega) = \frac{\omega^2 \Omega}{2\pi^2}\left(\frac{1}{C_l^3} + \frac{2}{C_t^3}\right) \tag{4.92}$$

The cut-off frequency ω_D is defined by (4.82) so that

$$\left(\frac{1}{C_l^3} + \frac{2}{C_t^3}\right)\frac{\Omega}{2\pi^2} = \frac{9N^3}{\omega_D^3}. \tag{4.93}$$
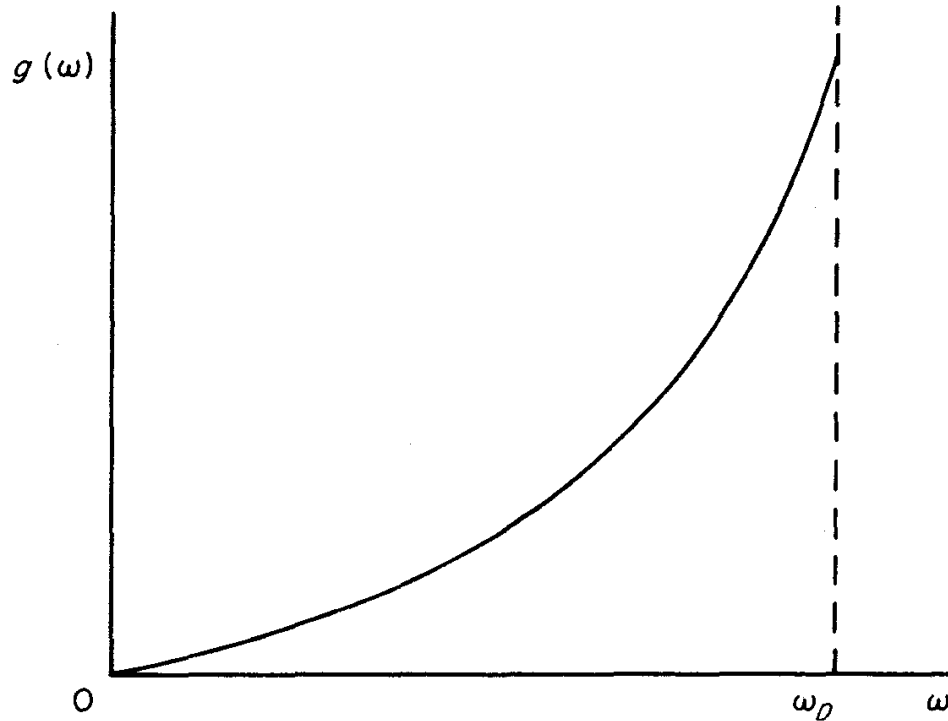
FIG. 4.16 Debye frequency distribution

Note that there is a common cut-off frequency for all three branches and so the longitudinal and transverse branches have different cut-off wavelengths.

From Brillouin zone theory it would seem more appropriate for the branches to have the same cut-off wavelength and hence different frequencies. Brillouin discusses this in his book *Wave Propagation in Periodic Structures*. The internal energy is from (4.83), (4.92) and (4.93).
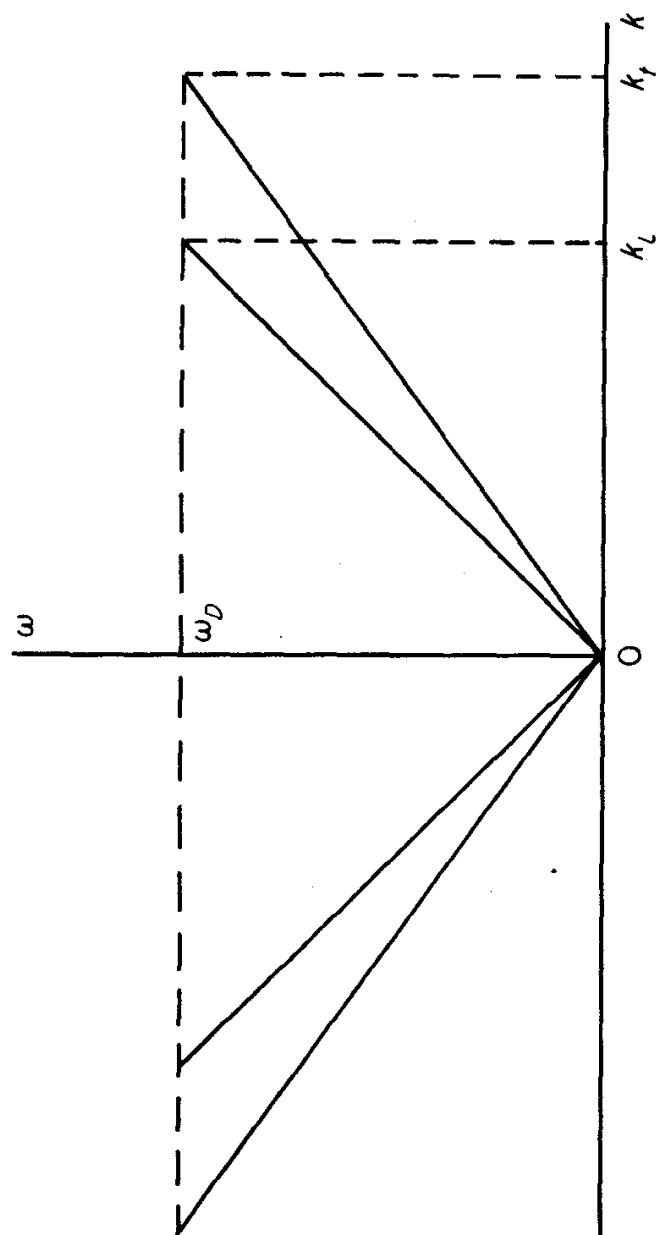
FIG. 4.17   Debye spectrum

$$U = \frac{9N^3}{\omega_D{}^3} \int_0^{\omega_D} \hbar\omega^3 \left[\frac{1}{e^{\hbar\omega/kT} - 1} + \tfrac{1}{2} \right] d\omega \qquad (4.94)$$

and the Debye heat capacity is

$$C_v = 3N^3 k 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx \qquad (4.95)$$

where the Debye temperature is defined by $\hbar\omega_D = k\,\theta_D$. The integral (4.95) can not be expressed in terms of known functions but has been tabulated (Landolt–Börnstein tables).
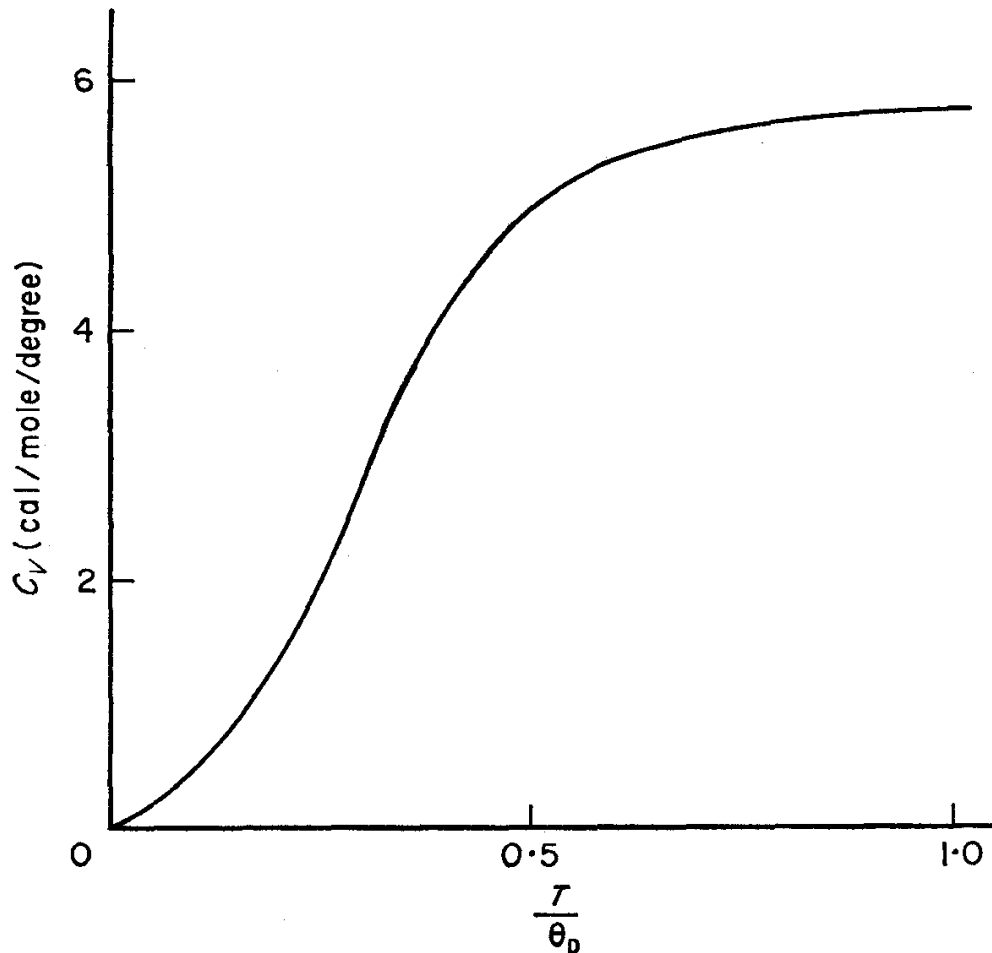
FIG. 4.18   Debye heat capacity

θ_D may be calculated by a suitable average of sound velocities (Blackman, 1941) and is not really as simple as (4.93) would imply. It is not difficult to see that the Dulong–Petit law (4.79)

is reproduced at high temperatures. Of course the correct T^3 variation is given at very low temperatures when $T << \theta_D$. At these low temperatures only the long wavelength modes are excited (4.80) and for these the Debye distribution is exact. If the upper limit on the integral is made infinite

$$C_v \simeq 3N^3k \left(\frac{T}{\theta_D}\right)^3 \frac{4\pi^4}{5} \qquad T << \theta_D \qquad (4.96)$$

At intermediate temperatures the fit is not so good. A standard test for the accuracy of the Debye specific heat function (4.95) is to calculate θ_D at different temperatures from the observed heat capacity. If the Debye theory was exact θ_D would be a constant. Often the variation in the Debye temperature is as little as 20%.

§ 4.10 Anharmonic effects

There are important phenomena for which it is necessary to consider the cubic terms in the potential function expansion (4.27). Examples are:

    (a) thermal expansion
    (b) thermal conductivity and
    (c) specific heat at high temperatures.

In the harmonic approximation, the mean displacement of the atoms from their positions of equilibrium is zero. When the cubic terms are included it is found that there is an average displacement proportional to the absolute temperature. (See Kittel's *Introduction to Solid State Physics*.)

Also, in the harmonic approximation the lattice waves travel freely without attenuation. This does not happen in reality owing to anharmonic terms and also due to crystal imperfections. The phonons interact with each other.

At high temperatures $(T > \theta_D)$ the specific heat deviates slightly from the Dulong–Petit value in that it includes a linear

term. This may be accounted for by considering the cubic and quartic terms in the potential expansion.

The reader is referred to Peierls' book *Quantum Theory of Solids* for further discussion.

Problems for Chapter 4

1. Write down the one-dimensional analogue of equation (4.28). The force on the nth particle is obtained by taking the negative derivative of the potential energy with respect to the displacement x_n. Hence obtain

$$m\ddot{x}_n = -\sum_m f_{nm} x_m$$

By considering the forces between particles explain why

$$f_{nm} = f_{mn} = A(|n - m|)$$

and
$$\sum_m f_{nm} = 0$$

Assuming nearest neighbour interactions only, derive equation (4.4) with $2\alpha = A(0)$. Why is α positive?

2. Find an expression for the group velocity of the lattice waves in a line of identical atoms. Show that this velocity is zero at the edges of the Brillouin zone. (In a lattice with no absorption the group velocity is equal to the 'energy velocity'.)

3. Consider a line of four equally spaced particles of equal mass m, the end ones being in fixed positions. Write down the equations of motion for longitudinal vibrations of the two free particles assuming that the force between any two is proportional to their relative displacement and that nearest neighbours only need be considered. Show that the angular frequencies of the two normal modes are in the ratio.

$$\frac{\omega_1^2}{\omega_2^2} = \frac{3}{1}$$

Write down expressions for the kinetic and potential energies and verify that the mass weighted normal co-ordinates are

$$Q_1 = \sqrt{\frac{m}{2}}(x_1 - x_2) \qquad Q_2 = \sqrt{\frac{m}{2}}(x_1 + x_2)$$

where x_1 and x_2 are the displacements of the two free particles.

4. The energy of a classical one-dimensional harmonic oscillator with angular frequency ω is

$$E = \frac{p^2}{2m} + \frac{m}{2}\omega^2 x^2$$

where m and p are the mass and momentum of the particle. When in thermal equilibrium the average energy of the oscillator is

$$\bar{E} = \int\!\!\int E \exp\,(-E/kT)\,\mathrm{d}p\,\mathrm{d}x\Big/\int\!\!\int \exp\,(-E/kT)\,\mathrm{d}p\,\mathrm{d}x$$

The integration is over phase space. Show that $\bar{E} = kT$. (You may use $\displaystyle\int_{-\infty}^{\infty} x^2 e^{-x^2}\,\mathrm{d}x = \sqrt{\pi}/2$ and $\displaystyle\int_{-\infty}^{\infty} e^{-x^2}\,\mathrm{d}x = \sqrt{\pi}$.

5. Consider one branch of the frequency spectrum. The locus of all points in the Brillouin zone with a given frequency is called a constant frequency surface. Explain why the spacing between two such surfaces with frequencies ω and $\omega + \mathrm{d}\omega$ is $\mathrm{d}k = \mathrm{d}\omega/|\,\mathrm{grad}_k\omega\,|$. From equation (4.74) the density of allowed k-values is $\Omega/(2\pi)^3$ where Ω is the crystal volume. Show that the frequency distribution is

$$g(\omega) = \frac{\Omega}{(2\pi)^3}\int\!\!\int \frac{1}{|\mathrm{grad}_k\omega\,|}\,\mathrm{d}S$$

where the integration is over the surface of constant frequency. One approximation for the frequency in the vicinity of the bottom of an acoustical branch is

$$\omega = \gamma(k_x^2 + k_y^2 + k_z^2)^{\frac{1}{2}}$$

Show that $g(\omega)\alpha\omega^2$ and determine the constant of proportionality. (Compare equation (4.91) in the Debye model.)

6. Consider a nondegenerate branch of the lattice spectrum. As ω^2 is an eigenvalue of a matrix whose elements are analytic then ω^2 is also analytic, i.e. ω^2 is continuous and has continuous derivatives. Write down the relation between $\text{grad}_k\omega^2$ and $\text{grad}_k\omega$. Show that the group velocity is necessarily zero at a maximum or minimum of ω^2 except at the bottom of the acoustical branches (Fig. 4.10). Employ the periodicity of ω^2 in k-space to deduce that the normal component of $\text{grad}_k\omega$ is zero at the boundary of the Brillouin zone. (This last result is not true if two branches are degenerate at the zone boundary.)

7. Consider a monatomic solid. A model similar to Debye's for calculating the lattice specific heat is as follows. It is again assumed that the phase velocity in a given branch is a constant and that the transverse branches are degenerate. Suppose a unique cut-off wavelength is defined by replacing the Brillouin zone by a sphere of equal volume. Then different cut-off frequencies are defined for the longitudinal and transverse branches so that each branch has N^3 modes. (In the Debye model the imposed condition is that the sum of all modes is $3N^3$.) Define characteristic temperatures θ_l and θ_t for both the longitudinal and transverse branches and show that the internal energy is

$$U = (N^3 k)\, T\left[D\left(\frac{\theta_l}{T}\right) + 2D\left(\frac{\theta_t}{T}\right) \right]$$

where

$$D(y) = \frac{3}{y^3}\int_0^y \left[\frac{1}{e^x - 1} + \tfrac{1}{2} \right] x^3 \, dx$$

8. Consider a pair of atoms. You may assume that when the atoms are displaced a distance x from their equilibrium separation the potential energy is,

$$V(x) = ax^2 - bx^3 - cx^4$$

Explain the significance of the terms in this expansion. The average displacement at a temperature T is

$$\bar{x} = \int_{-\infty}^{\infty} x e^{-V/kT} dx \Big/ \int_{-\infty}^{\infty} e^{-V/kT} dx$$

Show that for small displacements $\bar{x} = 3kTb/4a^3$. (You may use the integrals given in Problem 4.) Note that the anharmonic terms are necessary for a non-zero thermal expansion.

9. The Schrödinger equation for a one-dimensional harmonic oscillator of mass m and frequency ω is

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2}{2}x^2\right)\psi = E\psi$$

By a suitable transformation of the form $x = ky$ (k constant) obtain

$$\frac{d^2\psi}{dy^2} + (A - y^2)\psi = 0 \qquad A \text{ constant}$$

Quadratically integrable solutions exist only if $A = 1 + 2n$ where n is a positive integer and the solutions are multiples of the Hermite functions $\Psi_n(y)$.

These are orthogonal and satisfy

$$\int_{-\infty}^{\infty}\Psi_n\Psi_n\,dy = 2^n n!\sqrt{\pi}$$

Given the recurrence relations

$$2n\Psi_{n-1} = y\Psi_n + \Psi_n'$$

$$2y\Psi_n = 2n\Psi_{n-1} + \Psi_{n+1}$$

show that

$$\int_{-\infty}^{\infty}\Psi_m y\Psi_n\,dy = \begin{cases} 0 & m \neq n \pm 1 \\ 2^n(n+1)!\sqrt{\pi} & m = n+1 \\ 2^{n-1}(n)!\sqrt{\pi} & m = n-1 \end{cases}$$

and

$$\int_{-\infty}^{\infty}\Psi_m \Psi_n'\,dy = \begin{cases} 0 & m \neq n \pm 1 \\ -2^n(n+1)!\sqrt{\pi} & m = n+1 \\ 2^{n-1}(n)!\sqrt{\pi} & m = n-1 \end{cases}$$

Multiply $\Psi_n(y)$ by a suitable constant to normalize the wavefunction $\psi(x)$ to unity and confirm the matrix representations (4.66).

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5

Electron Energy Bands in Solids

§ 5.1 Introduction

The lattice periodicity of a crystal has important consequences for the dynamics of the electrons. At infinite separation, N atoms considered as a system, have the same energy levels as a single atom except that the degeneracy of each level is multiplied by N. As the atoms are brought together to form a crystal the degeneracy of the levels is removed by interactions. Each level of the isolated atom spreads out to form a band of allowed electron energies. Between the bands there may occur forbidden energy gaps. The resulting band structure to a large extent determines the electrical properties of the crystal.

From an electrical viewpoint a material may be classified as a metal, semiconductor or an insulator by the value of its resistivity. At room temperature metals have a resistivity of about 10^{-6} ohm cm, semiconductors have values in the range $10^{-2} \sim 10^{8}$ ohm cm, and insulators have resistivities greater than about 10^{10} ohm cm. The main factors which decide this classification for a material are the valencies of the constituent atoms and the magnitude of the energy gaps between the bands.

§ 5.2 The reciprocal lattice

Each Bravais lattice has an associated reciprocal lattice, defined by the three basis vectors b_1, b_2 and b_3 with

$$b_j \cdot a_i = 2\pi \delta_{ij} \qquad (5.1)$$

a_1, a_2, a_3 are the basis vectors of the direct (Bravais) lattice. Vectors b_i that satisfy these relations are

$$b_1 = \frac{2\pi}{V_d}(a_2 \wedge a_3), \quad b_2 = \frac{2\pi}{V_d}(a_3 \wedge a_1) \qquad (5.2)$$

$$b_3 = \frac{2\pi}{V_d}(a_1 \wedge a_2)$$

where $V_d = a_1 \cdot (a_2 \wedge a_3)$ is the volume of the primitive cell of the direct lattice.

The reciprocal lattice is composed of the end-points of all the vectors

$$K_m = m_1 b_1 + m_2 b_2 + m_3 b_3 \qquad (5.3)$$

$$m_1, m_2, m_3 \text{ integers}$$

The primitive cell has a volume

$$V_b = b_1 \cdot (b_2 \wedge b_3) \qquad (5.4)$$

and it can be shown that

$$V_b = (2\pi)^3/V_d \qquad (5.5)$$

A function $f(r)$ which is periodic with the period of the direct lattice may be expanded in a Fourier series in the reciprocal lattice vectors K_m. To see this observe that the reciprocal lattice vectors have the important property

$$K_m \cdot R_n = 2\pi l \qquad (5.6)$$

with l an integer or zero. The converse of (5.6) is also true. That is if a vector K is such that the scalar product $K \cdot R_n$ is an integral multiple of 2π for all R_n then K is a reciprocal lattice vector. If $f(r)$ is given by

$$f(r) = \sum_{K_m} A_m e^{iK_m \cdot r} \qquad (5.7)$$

then

$$f(r + R_n) = \sum_{k_m} A_m e^{iK_m \cdot (r + R_n)}$$

and as

$$e^{iK_m \cdot R_n} = 1$$

then

$$f(r + R_n) = f(r)$$

The reciprocal lattice of a reciprocal lattice is the original direct lattice. This can be verified by considering the vector
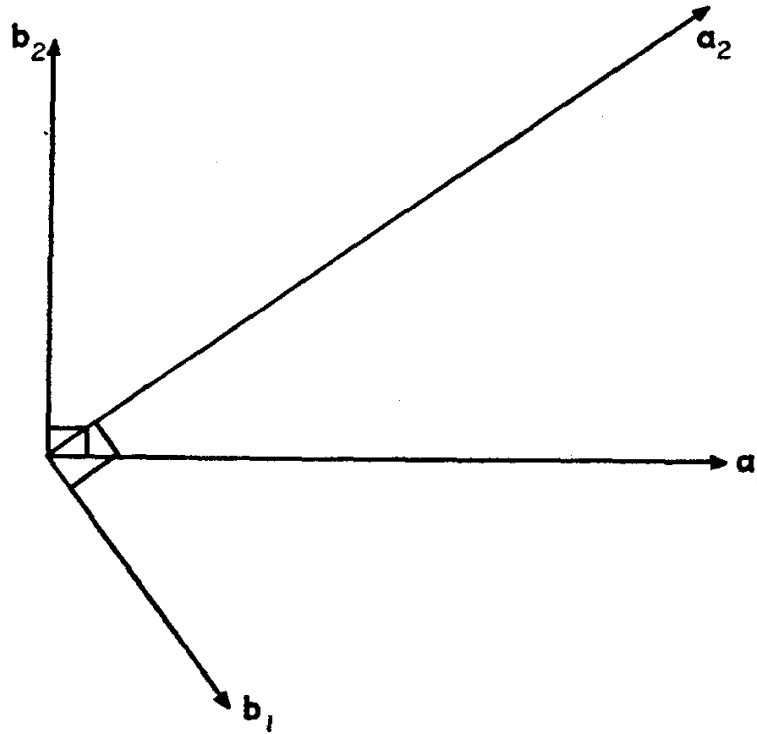
a_3(also b_3) out of the paper

FIG. 5.1   Direct and reciprocal lattice vectors

$2\pi(b_2 \wedge b_3)/V_b$ and showing that it is equal to a_1. From (5.2)

$$\frac{2\pi}{V_b}(b_2 \wedge b_3) = \frac{1}{V_d}(a_3 \wedge a_1) \wedge (a_1 \wedge a_2)$$

$$= \frac{1}{V_d}\{(a_1 \cdot a_2 \wedge a_3)a_1 - (a_1 \cdot a_2 \wedge a_1)a_3\}$$

$$= a_1$$

The reciprocal lattice is invariant under the same point group as the direct lattice. For if α is a point group symmetry operation which leaves the direct lattice invariant then αR_n is a lattice translation if R_n is. From (5.6)

$$K_m \cdot (\alpha R_n) = 2\pi l \qquad l \text{ interger}$$

i.e.

$$(\alpha^{-1} K_m) \cdot R_n = 2\pi l$$

The latter equation shows that $(\alpha^{-1} K_m) \cdot R_n$ is an integral multiple of 2π for all R_n and so $(\alpha^{-1} K_m)$ is a reciprocal lattice vector.

This final result demands that a direct lattice and its reciprocal lattice belong to the same crystal system. In fact ten of the fourteen Bravais lattices are their own reciprocals. Examples which are not are the face-centred cubic and body-centred cubic lattices which are the reciprocals of each other.

§ 5.3 The Bloch theorem and energy bands

One-dimensional lattice

This central theorem shows how the allowed energy eigenstates of a perfect crystal may be classified by a real wave vector k and will first be proved for the one-dimensional case. Later a group theoretical proof will be given for three-dimensional lattices.

The Schrödinger equation for a line of identical atoms is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \qquad (5.8)$$

with

$$V(x - a) = V(x)$$

Suppose $\psi_1(x)$ and $\psi_2(x)$ are two real linearly independent solutions each satisfying prescribed boundary conditions and belonging to the energy E. Any other solution with energy E may be expressed as a linear combination of them and in particular $\psi_1(x - a)$ and $\psi_2(x - a)$ are solutions with

$$\psi_1(x - a) = \alpha_{11}\psi_1(x) + \alpha_{12}\psi_2(x) \qquad (5.9)$$
$$\psi_2(x - a) = \alpha_{21}\psi_1(x) + \alpha_{22}\psi_2(x)$$
$$\alpha_{ij} \text{ real}$$

If the ψ_1 Schrödinger equation is multiplied by ψ_2 and the ψ_2 equation by ψ_1 then subtracted and the result integrated by parts then

$$W(x) \equiv \psi_1 \frac{d\psi_2}{dx} - \psi_2 \frac{d\psi_1}{dx} = \text{constant} \qquad (5.10)$$

$W(x)$ is the Wronskian of the solutions. From (5.9) and (5.10)

$$W(x - a) = (\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21})W(x) \qquad (5.11)$$

and so $\qquad\qquad (\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21}) = 1$

It is possible to find solutions ϕ which are linear combinations of ψ_1 and ψ_2 so that they are multiplied by a constant on translation by a.

i.e. $\qquad \phi = \beta_1\psi_1 + \beta_2\psi_2 \qquad \beta_1, \beta_2$ may be complex

with $\qquad\qquad \phi(x - a) = \lambda\phi(x) \qquad\qquad (5.12)$

λ is a constant. From (5.12) and (5.9)

$$(\alpha_{11} - \lambda)\beta_1 + \alpha_{21}\beta_2 = 0$$
$$\alpha_{12}\beta_1 + (\alpha_{22} - \lambda)\beta_2 = 0$$

The condition for a non-trivial solution is

$$\begin{vmatrix} \alpha_{11} - \lambda & \alpha_{21} \\ \alpha_{12} & \alpha_{22} - \lambda \end{vmatrix} = 0$$

i.e. $\qquad\qquad \lambda^2 - \lambda(\alpha_{11} + \alpha_{22}) + 1 = 0$

The product of the two roots of this quadratic is unity and as $(\alpha_{11} + \alpha_{22})$ is real their sum is real. A real function of the energy is defined by

$$\mu(E) = \tfrac{1}{2}(\alpha_{11} + \alpha_{22}) = \frac{\lambda_1 + \lambda_2}{2}$$

where λ_1 and λ_2 are the two roots. It is convenient to write

$$\lambda_1 = e^{-ika} \qquad \lambda_2 = e^{ika}$$
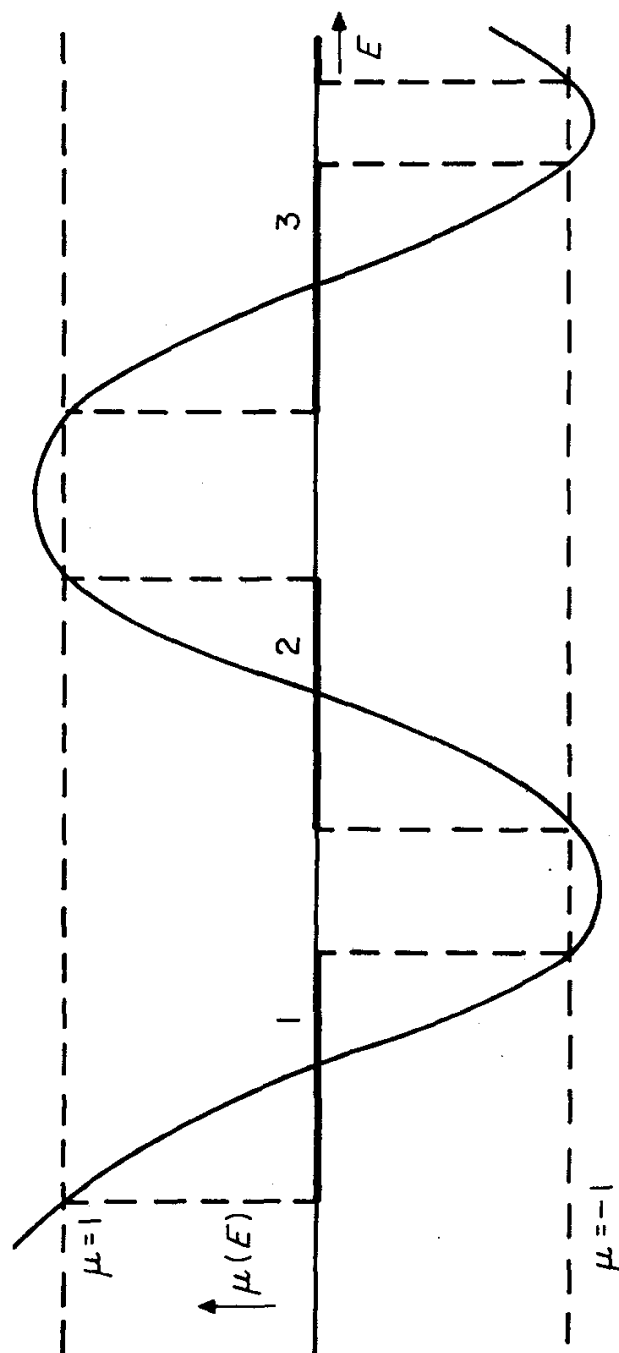
FIG. 5.2 $\mu(E)$ curve. The allowed energy bands correspond to $|\mu| \leqslant 1$

where k is not necessarily real. Then

$$\mu(E) = \cos ka$$

There are three distinct cases to consider.

(i) $$\qquad |\mu(E)| > 1$$

k is not real but the roots of the quadratic are real.

$$\lambda_1 = \pm e^{\beta a} \qquad \lambda_2 = \pm e^{-\beta a}$$
$$\beta \text{ real}$$

Both these solutions are divergent for an infinite crystal and do not represent allowed eigenstates.

(ii) $$\qquad |\mu(E)| < 1$$

k is real and the roots are complex and lie on the unit circle in the complex plane. They represent allowed eigenstates and the wave functions are denoted by k and are called Bloch waves.

$$\psi_k(x - a) = e^{-ika}\psi_k(x) \qquad (5.13)$$

This is the Bloch theorem. Note that the states for $\pm k$ are degenerate and that k is defined only to within a multiple of $2\pi/a$. It is conventional to restrict k to lie in the range $-\pi/a < k \leqslant \pi/a$ and there will be a series of wave functions for each k transforming as in (5.13) but with different energies.

(iii) $$\qquad |\mu(E)| = 1$$

In this case the quadratic has a double root equal to ± 1. This is an allowed solution.

Kramers (1935) studied the form of $\mu(E)$ for a non-degenerate band (Fig. 5.2).

In particular

$$\lim_{E \to -\infty} \mu(E) = + \infty$$

$$\mu(E) \longrightarrow \cos(a\sqrt{E}) \text{ as } E \longrightarrow \infty$$

In between these limits $\mu(E)$ oscillates between values greater than one and less than one and so there are alternate allowed

and forbidden bands of energy. This essential property is maintained in three-dimensional crystals.

Three-dimensional lattice

A rather different approach will now be used to prove Bloch's theorem for a three-dimensional lattice. The one-electron Schrödinger Hamiltonian is

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \qquad (5.14)$$

The crystal potential $V(r)$ is unchanged if the point of observation is displaced by a lattice vector R_n.

$$V(r - R_n) = V(r) \qquad (5.15)$$

$$R_n = n_1 a_1 + n_2 a_2 + n_3 a_3 \qquad n_1, n_2, n_3 \text{ integers}$$

The substitutional operator representing this translation is $\{\epsilon \mid R_n\}$.

$$\{\epsilon \mid R_n\}V(r) = V(r - R_n) \qquad (5.16)$$

For an infinite crystal the number of lattice translations is infinite. A real finite crystal is of course not truly invariant under $\{\epsilon \mid R_n\}$ but if surface effects are negligible it may be taken to be so. To simplify the discussion it is convenient to keep the number of distinct translations finite by the introduction of periodic boundary conditions.

Consider a microcrystal of size Na_1 by Na_2 by Na_3. Two points of view may be taken. Either consider an infinite number of identical microcrystals stacked together or imagine opposite sides of the crystal to be joined in some sense. The latter viewpoint is easily conceived in one-dimension in the form of a ring of atoms or in two dimensions as a torus surface but there is no such physical picture in three dimensions. The three translations Na_1, Na_2, Na_3 are considered to produce no change at all.

$$\{\epsilon \mid 0\} = \{\epsilon \mid Na_1\} = \{\epsilon \mid Na_2\} = \{\epsilon \mid Na_3\} \qquad (5.17)$$

The periodic boundary conditions may be used whenever in-

terior properties of crystals are studied and the surface to volume ratio is very small.

The translation operators now form a finite group of N^3 elements. This group is of course a sub-group of the full crystal space group. The translations commute with one another, so forming an Abelian group, and consequently all the irreducible representations are one-dimensional and the number is equal to the order of the group N^3.

Clearly the Hamiltonian is invariant under the translation group and so the energy eigenfunctions must transform according to one of the irreducible representations of the group. Another way of stating this is to say that the Hamiltonian and the translation operators commute with each other and so wave functions may be chosen to be simultaneously eigenfunctions for $\mathcal{H}$ and all the operators $\{\epsilon \mid R_n\}$.

Let ψ be the basis for one of the irreducible representations

$$\{\epsilon \mid a_i\}\psi(r) = \lambda_i \psi(r) \qquad i = 1, 2, 3 \qquad (5.18)$$

where λ_i are constants which may be complex. The periodic boundary conditions demand

$$\lambda_1^N = \lambda_2^N = \lambda_3^N = 1 \qquad (5.19)$$

Each λ_i must be one of the N roots of unity.

$$\lambda_i = e^{-i2\pi r_i/N} \qquad r_i = 1, 2, \ldots, N \qquad (5.20)$$

For a general translation $\{\epsilon \mid n_1 a_2 + n_2 a_2 + n_3 a_3\}$ λ is given by

$$e^{-i\frac{2\pi}{N}(r_1 n_1 + r_2 n_2 + r_3 n_3)} \qquad (5.21)$$

This may be written $e^{-ik \cdot R_n}$ where the real 'wave vector' k takes the discrete values

$$k = \frac{1}{N}(r_1 b_1 + r_2 b_2 + r_3 b_3) \qquad r_i = 1, 2, \ldots, N$$

$$(5.22)$$

b_1, b_2, b_3 are the reciprocal lattice basis vectors. These k-values

lie very close together and for many purposes are taken to form a continuum.

In this way, the irreducible representations and hence the energy eigenfunctions may be characterized by a wave vector and for these functions

$$\{\epsilon \mid R_n\}\psi_k(r) = e^{-ik \cdot R_n}\psi_k(r) \tag{5.23}$$

This is Bloch's famous theorem.

A function satisfying this condition is

$$\psi_k(r) = e^{ik \cdot r}u_k(r) \tag{5.24}$$

if $u_k(r)$ has the lattice periodicity.

If the wave vector of an eigenstate is defined by (5.24) then it is obvious (from (5.6)), that k is not unique since k and $k + K_m$ are equivalent.

$$e^{iR_n(k + K_m)} = e^{iR_n \cdot k} \text{ for all } R_n \tag{5.25}$$

To label k uniquely it is necessary to restrict k to a reciprocal
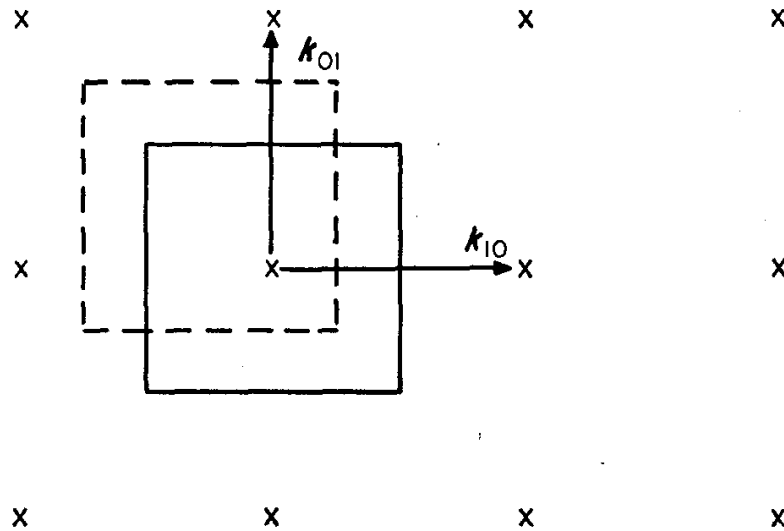
FIG. 5.3   Brillouin zones of square reciprocal lattice. The dotted square shows an alternative primitive cell

lattice primitive cell. This value of k is called the reduced wave vector. The symmetric primitive cell, called the Brillouin zone, is obtained by bisecting the lines joining $k = 0$ to the nearest reciprocal lattice points. The analogous cell in the direct lattice

is the Wigner–Seitz cell. Each point exterior to the Brillouin zone is equivalent to some interior point in the sense of (5.25) and similarly, a point on the surface of the zone will be equivalent to at least one other point on the surface.

There are N^3k-vectors of the type (5.22) inside the Brillouin zone and this gives correctly the total number of distinct irreducible representations of the translation group.
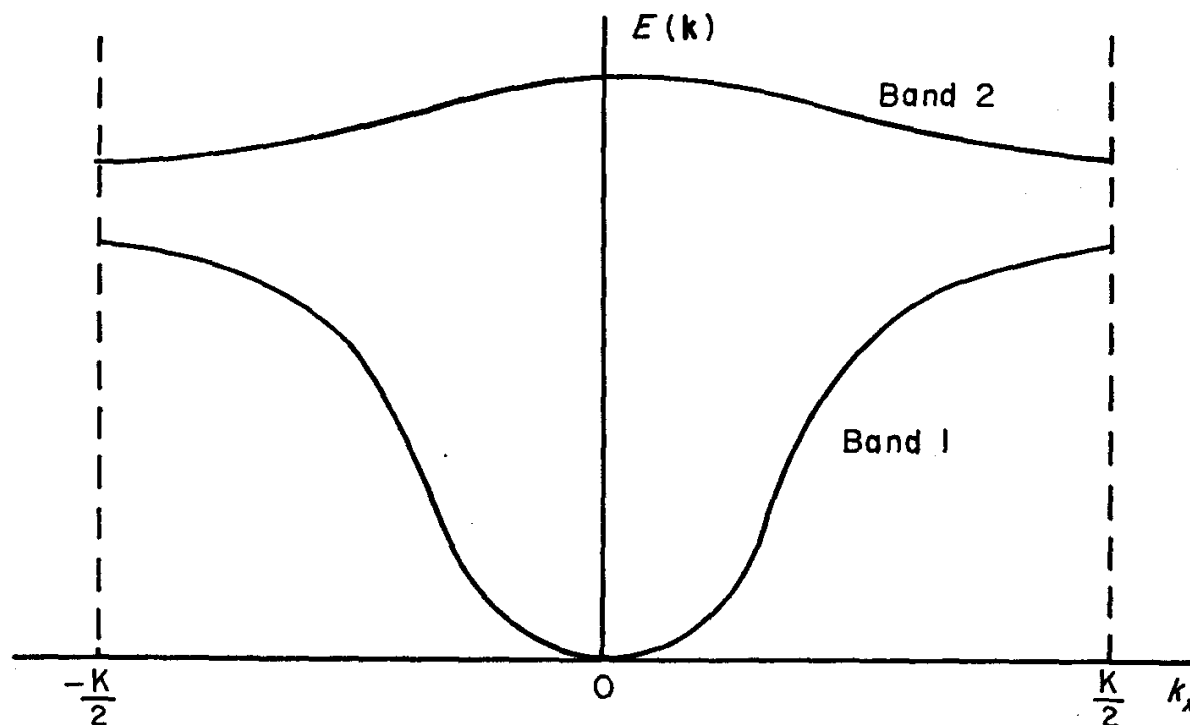
FIG. 5.4   Energy band structure

The energies of the electron states may be regarded as a function of the 'quasi-continuous' k-vector. In this reduced zone scheme, this function is multi-valued and is normally written $E_n(k)$, n denoting the branch. It may be shown that within the Brillouin zone, the energy is a continuous function of k with a continuous derivative. A single continuous branch is called an energy band. Discontinuities in the energy may occur only on the surface of the zone.

The restriction of k to lie within the Brillouin zone is only a convention. Alternatively k may be allowed to take all values

and then the energy $E(k)$ will be a periodic (still multivalued) function of k.

$$E_n(k) = E_n(k + K_n) \qquad (5.26)$$

If the periodic boundary condition is relaxed then there are other possible irreducible representations. The operator $\{\epsilon \mid R_n\}$ may be represented by $e^{\mu \cdot R_n}$ where μ is a complex constant vector depending upon the basis function.

$$\{\epsilon \mid R_n\}\psi_\mu(r) = e^{\mu \cdot R_n}\psi_\mu(r)$$

The commutation relations of the translation group are satisfied, but these solutions do not correspond to physically acceptable wave functions as they diverge. The eigenfunctions in the energy gap between bands are of this form.

The major problem in band theory is to find as good an approximation as possible to $E(k)$. An important quantity that can be derived is the density of states $N(E)$ defined so that $N(E)\,dE$ is the number of states in a band in the range E to $E + dE$. Consider a surface in k-space on which the energy has the constant value E and construct a right cylinder with base area dS on this surface and with length dk. The number of states in this cylinder is (5.22) $\Omega\,dk\,dS/(2\pi)^3$ where Ω is the crystal volume. As $dk = dE/|\operatorname{grad}_k E|$ then the number of states per unit energy is

$$N(E) = \frac{\Omega}{(2\pi)^3} \iint \frac{1}{|\operatorname{grad}_k E|}\,dS \qquad (5.27)$$

where the integration is over the surface of constant energy. Each of these states may be occupied by two electrons. Clearly $N(E)$ may have a singularity when the integration includes a point at which $|\operatorname{grad}_k E| = 0$. These are called critical points and their occurrence has been studied by Morse (1938) and van Hove (1953 — lattice spectrum). There are four types of analytic critical points about which the energy can be expressed as a Taylor series in k with the first derivative terms omitted. These are a maximum, minimum and two kinds of
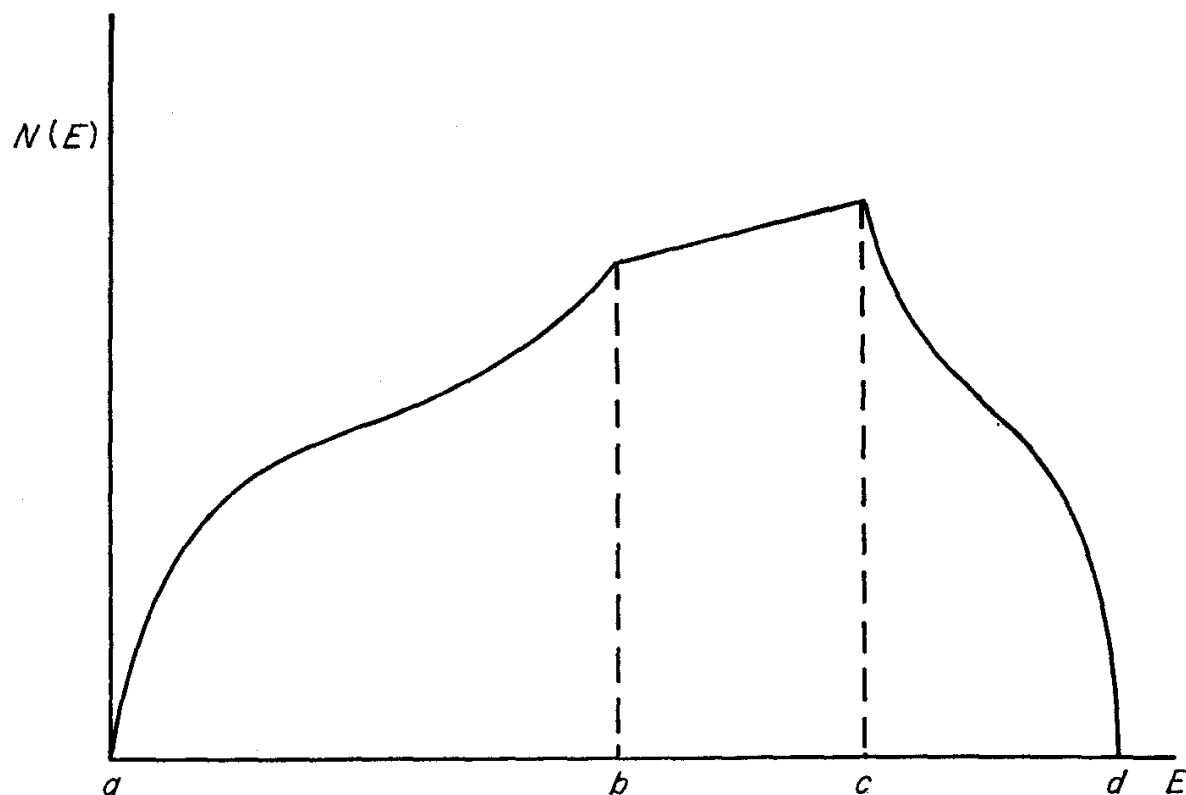
(a) — Minimum $N(E) \alpha E^{1/2}$

$\left.\begin{array}{l} \text{(b)} \\ \text{(c)} \end{array}\right\}$ — Saddle points — discontinuity in slope

(d) — Maximum $N(E) \alpha (E_d - E)^{1/2}$

FIG. 5.5   Singularities in the density of state function

saddle point. It can be shown that a non-degenerate band must include singularities of all four types.

§ 5.4 Symmetry properties of the energy function

The operations which carry a crystal into itself form the space group. The Seitz notation for a general rotation-translation operator is $\{\alpha \mid t\}$ and has previously been discussed (3.8–3.11). t is not necessarily restricted to the lattice translations. For

crystals possessing screw axes or glide planes, t may be a fractional lattice displacement.

The point group of a crystal is the collection of rotations (inversions or reflections) α, which appear in the elements of the space group. There may exist rotations α' which always occur in the form $\{\alpha' \mid t'\}$ where t' is not a primitive translation. Even though $\{\alpha' \mid 0\}$ is not a member of the space group the rotation α' is a member of the point group. It is quite possible that no atom site in a crystal has the full point group symmetry. For example, the point group of the diamond crystal is the full cubic group $m3m$ but the carbon atoms are in an environment with the reduced tetrahedral symmetry $\bar{4}3m$. Diamond, of course, has a screw axis. A space group which does not involve non-primitive translations is called symmorphic and in this case the point group is a sub-group of the space group.

In Section 5.3 it has been shown how the lattice periodicity means that the energy eigenfunctions may be specified by a wave-vector k. If the crystal point group contained only the identity (as in a triclinic lattice without even inversion symmetry) and the complex conjugation operator (Section 5.5) is ignored, then all the eigenstates would have different energies. In general though, the elements of the point group produce degeneracies between different k states.

The operator $\{\alpha \mid 0\}$ transforms a Bloch wave with vector k into the Bloch wave with vector αk. From (5.24)

$$\{\alpha \mid 0\}\psi_k(r) = e^{ik\cdot(\alpha^{-1}r)}u_k(\alpha^{-1}r) \qquad (5.28)$$

The scalar product $k \cdot (\alpha^{-1}r)$ is invariant if the same rotation is applied in both k-space and real space.

$$\therefore \qquad (\alpha k) \cdot r = k \cdot (\alpha^{-1}r)$$
$$\{\alpha \mid 0\}\psi_k(r) = e^{i(\alpha k)\cdot r}u_{\alpha k}'(r) = \psi_{\alpha k}(r) \qquad (5.29)$$

The function $U_{\alpha k}'$ maintains the lattice periodicity.

It is left to the reader to show that

$$\{\alpha \mid t\}\psi_k(r) = e^{i(\alpha k)\cdot r}u_{\alpha k}'(r) \qquad (5.30)$$

even in the case where t is not a primitive translation. The rotation-translation operators commute with the Hamiltonian and so all the wave functions given by $\{\alpha \mid t\}\psi_k$ must be degenerate with ψ_k. The energy spectrum in k-space must have the full point group symmetry.

$$E_n(k) = E_n(\alpha k) \qquad (5.31)$$

The wave vectors generated from k by the crystal point group form a set which is called the star of the k-vector.

For symmetry points in k-space $\alpha k = k$ for some point group operators. These operators form the 'small group' of that particular k. There is the possibility of degeneracies between bands at such symmetry points and then Bloch waves from the different bands must belong to an irreducible representation of the small group of k.

A simple two-dimensional example will help to clarify the above. A square direct lattice has a square reciprocal lattice. If a is the minimum repeating length in the real lattice then $2\pi/a$ is the minimum length in the reciprocal lattice. The Brillouin zone is a square of side $2\pi/a$.

The square point group is 4mm with eight elements. (See Fig. 3.10.) Each of these operations will take a general wave vector, say k_1 into a new position. The star will include the eight points k_1 to k_8 (Fig. 5.6). There are six types of special points in the zone. The point Γ at the centre of the zone with $k = 0$ has a small group identical with the square point group 4mm. The star of Γ is the single point $k = 0$. Degenerate Bloch functions at this point must transform according to one of the irreducible representations of the square group (Table 3.4). Consequently only singly or doubly degenerate states are possible.

Two elements of the square group, E, m_y leave the point Δ invariant and so form its small group. (The group m.) The remaining six elements produce the star of Δ consisting of four points on the positive and negative k_x, k_y axes.

At first glance it may appear that the point Z is left invariant only by the unit element E. This is not in fact true as Z and Z'
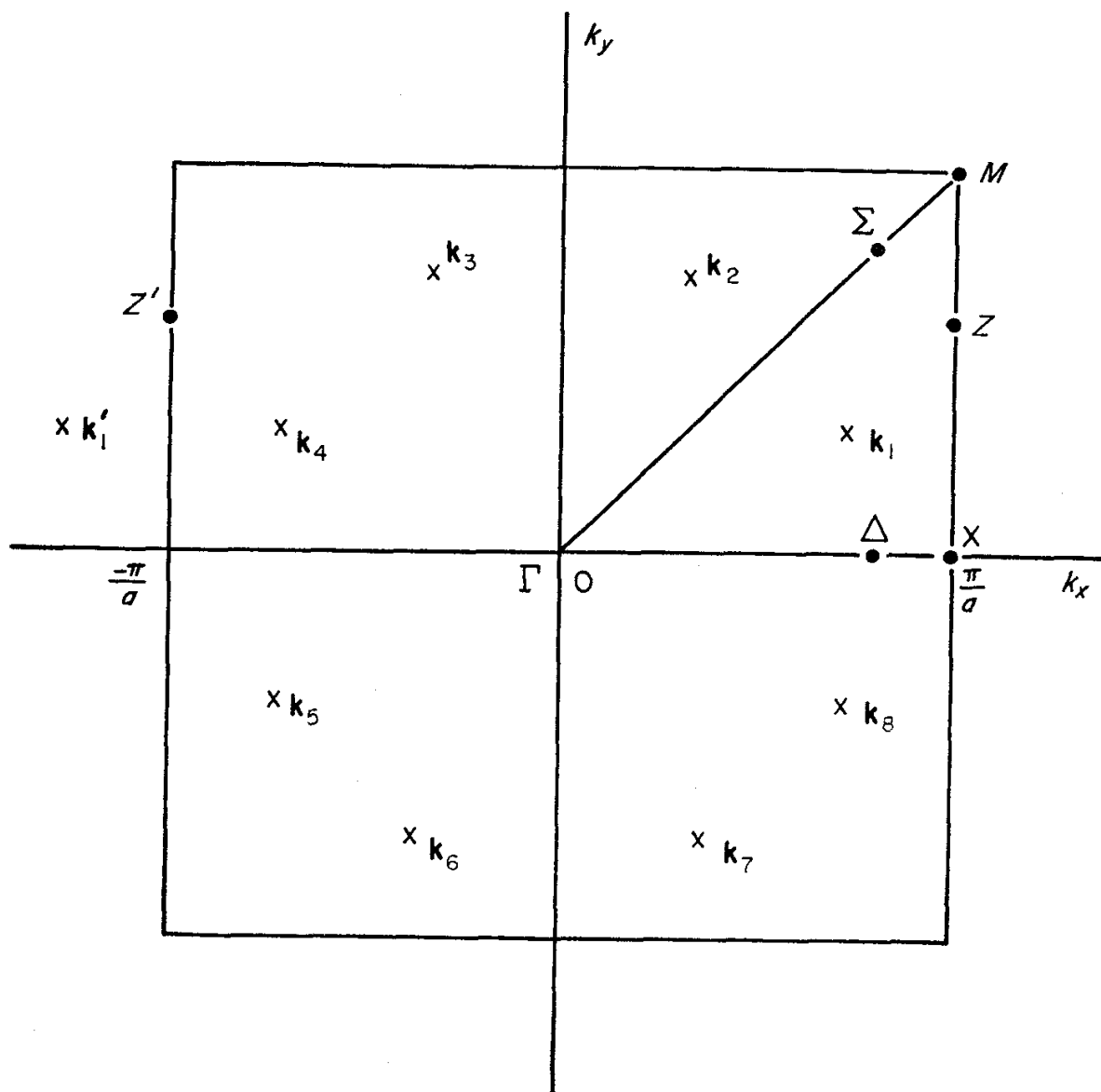
FIG. 5.6   Square lattice Brillouin zone

are really equivalent as they differ by a reciprocal lattice vector. The small group of Z consists of the two elements E, m_x.

It is left as a simple exercise to the reader to show that the small group of

M i 4mm with eight elements,
X is 2mm with four elements,
Σ is m with two elements.

Normal case

Crystal with glide plane or screw axis
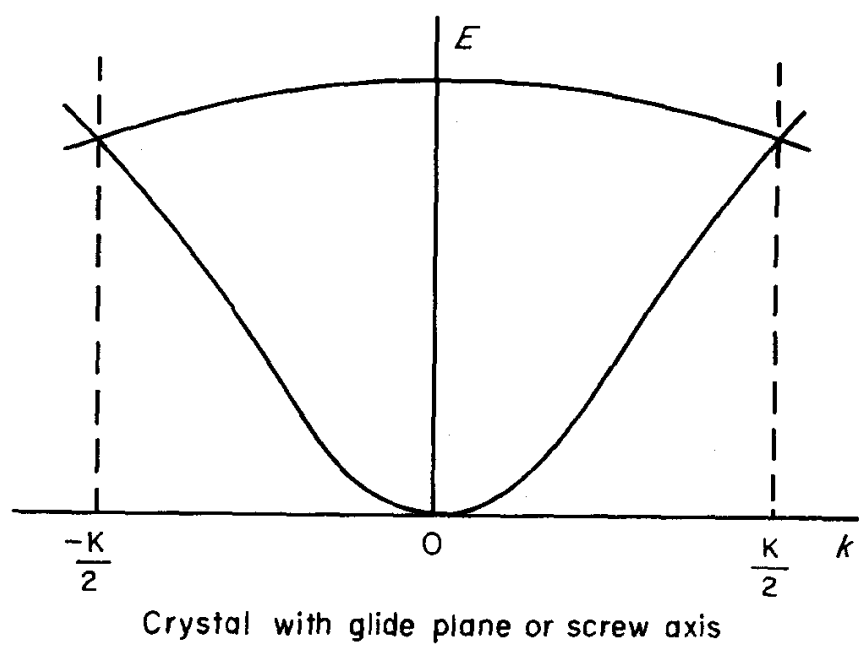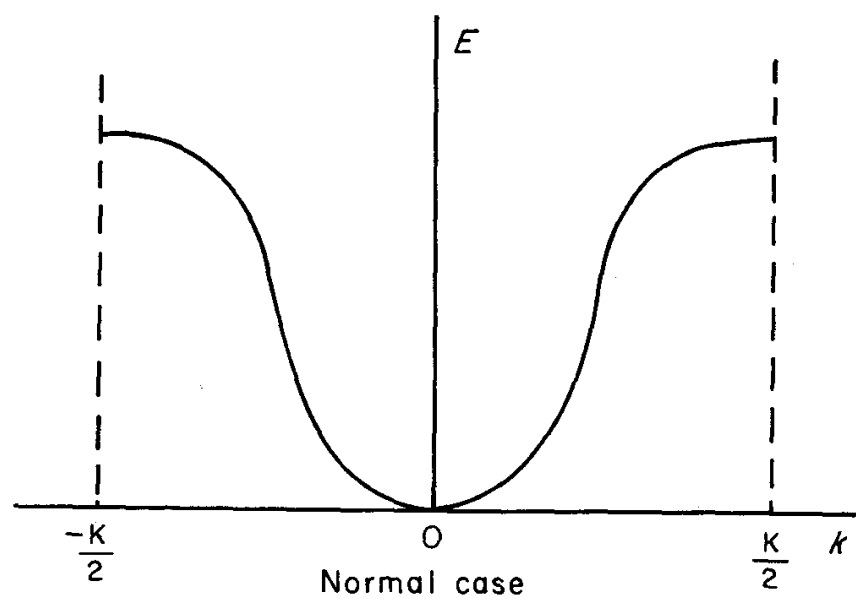
FIG. 5.7

It is easy to show that an energy band has a relative maximum or minimum as it crosses the zone boundary. The point k_1' is equivalent to k_1 and so

$$E(k_1') = E(k_1) = E(k_4)$$

It has already been mentioned that the energy function is continuous with a continuous derivative and so by taking k_1 close enough to the zone boundary the result is obvious. This means that, for the square lattice, the normal component of $\mathrm{grad}_k E(k)$ is zero on the zone boundary.

Often this result is true in three dimensions. If there is sufficient symmetry so that the two opposite sides of a Brillouin zone face are symmetrically equivalent then in general the normal component of $\mathrm{grad}_k E(k)$ is zero on the boundary. Possible exceptions arise when two bands stick together at a zone boundary. This may happen when a crystal contains screw axes or glide planes.

§ 5.5 The complex conjugation operator

If the crystal point group contains the inversion then clearly

$$E(k) = E(-k) \tag{5.32}$$

In fact, if spin is ignored it is an easy matter to show that this result is always true. The Schrödinger equation is a real differential equation and so if ψ_k is an eigenfunction with energy E then ψ_k^* belongs to the same energy.

$$\psi_k(r) = e^{ik \cdot r} u_k(r)$$
$$\psi_k^*(r) = e^{i(-k \cdot r)} u_{-k}'(r)$$

with
$$u_{-k}' = u_k^*$$

The complex conjugate function ψ_k^* has the same energy as ψ_k but transforms according to ψ_{-k}. The energy surfaces in k-space have inversion symmetry even if this symmetry is not included in the crystal point group.

In this spin-free case, each k-state may be filled by two electrons and so in fact each band is two-fold degenerate. When spin-orbit coupling is introduced, the situation is more complex and will not be considered further.

§ 5.6 Nearly free electron model

In this model the crystal potential $V(r)$ is assumed to be very weak compared with the electron kinetic energy. This does not correspond to the motion of valence electrons in any crystal as the variations of potential energy are generally comparable to the kinetic energy. Even so, the method is worth describing as it is one of the limiting cases (the other is tight-binding); and is the basis of more sophisticated approaches. (See O.P.W., etc.) The approximation will apply to the motion of a beam of fast electrons ejected into a crystal.

For simplicity, the one-dimensional case is discussed. It is convenient to choose the zero of energy so that the mean value of the potential function is zero.

i.e.
$$\int_0^a V(x)\, dx = 0 \qquad (5.33)$$

where a is the lattice period. With this choice of zero, V represents the variations of the potential energy. The Schrödinger equation to be solved is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi \qquad (5.34)$$

As V is assumed to be small compared with the kinetic energy, perturbation theory is employed.

The unperturbed wave functions corresponding to $V = 0$ are the plane waves

$$\phi_k(x) = \frac{1}{\sqrt{Na}}\, e^{ikx} \qquad (5.35)$$

These wave functions are normalized over a microcrystal containing N cells. The unperturbed electron energies are

$$E^0(k) = \hbar^2 k^2/2m \qquad (5.36)$$

Of course in the free electron model k takes all values. Suppose account is taken of the lattice 'structure' only by restricting k to lie in the Brillouin zone.

Then

$$\psi_k(x) = \frac{1}{\sqrt{Na}} e^{in\frac{2\pi}{a}} \cdot e^{ikx} \qquad E^0(k) = \frac{\hbar^2}{2m}\left(k + n\frac{2\pi}{a}\right)^2$$

$$|k| \leqslant \frac{\pi}{a} \qquad\qquad n \text{ integer}$$

The energy bands can be drawn straight away. This is the 'empty-lattice' test (Shockley, 1937). Observe that the bands do not join smoothly at the zone boundary.

When the small periodic potential is introduced the different plane waves are no longer independent. However, if V is weak it may be expected that each perturbed wave function is composed primarily of a single plane wave ϕ_k and so the real wave functions are labelled by k.

$$\psi_k = \phi_k + \sum_{k' \neq k} A_{k'}(k)\phi_{k'} \qquad (5.37)$$

From perturbation theory, the constants $A_{k'}(k)$ are small and correct to first order are given by

$$A_{k'}(k) = \frac{<k' \mid V \mid k>}{E^0(k) - E^0(k')} \qquad (5.38)$$

with $\qquad <k' \mid V \mid k> = \int \phi_{k'}^* V \phi_k \, dx \qquad (5.39)$

The perturbed energy, correct to second order is

$$E(k) = E^0(k) + \sum_{k'}' \frac{|<k' \mid V \mid k>|^2}{E^0(k) - E^0(k')} \qquad (5.40)$$

(The first order term is zero by virtue of (5.33).)
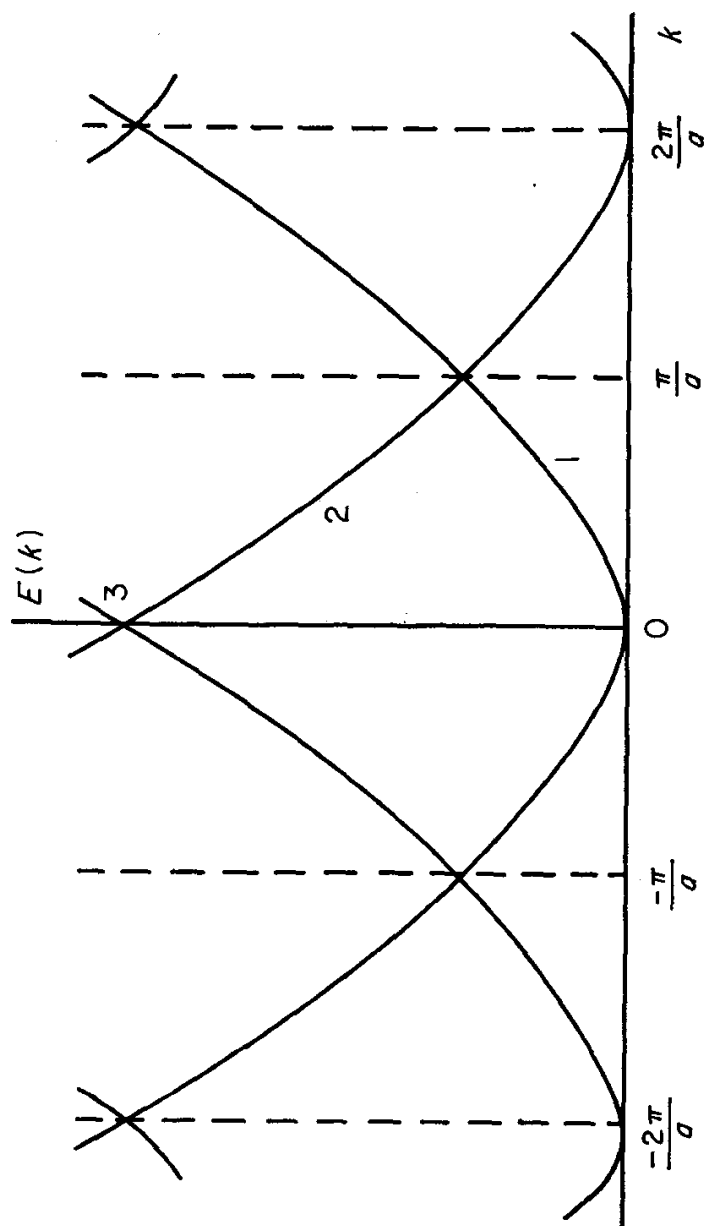
FIG. 5.8   Empty lattice test — linear lattice

The real periodic potential may be expressed as a Fourier series.

$$V(x) = \sum_{n \neq 0} V_n e^{-in\frac{2\pi}{a}x} \qquad n \text{ integer} \qquad (5.41)$$

$$V_n{}^* = V_{-n}$$

Clearly, the integral

$$<k' \mid V \mid k> = V_n \text{ if } k - k' = n\frac{2\pi}{a}$$

$$= 0 \text{ otherwise} \qquad (5.42)$$

The state k is mixed only with the states $k - n2\pi/a$ by the periodic perturbation. The new wave function is now seen to be

$$\psi_k(x) = e^{ikx}\left[\frac{1}{\sqrt{Na}} \sum_{n=0} A_n(k)e^{-in\frac{2\pi}{a}x}\right] \qquad (5.43)$$

with

$$A_0 = 1$$

$$A_n = \frac{V_n}{E^0(k) - E^0\left(k - n\frac{2\pi}{a}\right)} \qquad n \neq 0$$

The quantity in brackets is just the periodic part of the Bloch wave. The perturbed energy is

$$E(k) = E^0(k) + \sum_{n \neq 0} \frac{\mid V_n \mid^2}{E^0(k) - E^0\left(k - n\frac{2\pi}{a}\right)} \qquad (5.44)$$

This final expansion for the energy is satisfactory if the Fourier components V_n tend to zero rapidly as n increases and if there are no degeneracies among the plane wave states of the type

$$E^0(k) = E^0\left(k - n\frac{2\pi}{a}\right) \qquad (5.45)$$

The condition necessary for this type of degeneracy to occur is (from (5.36)),

$$\mid k \mid = \left| k - n\frac{2\pi}{a} \right| \qquad (5.46)$$

At or near a Brillouin zone boundary, where $k = n\pi/a$ the perturbation expansion is no longer valid. The perturbation method fails because it is no longer permitted to assume that A_n is small compared with unity (5.43). The incident and diffracted rays are now on an equal footing. Near a zone boundary it is necessary to write

$$\psi_k = A_0\phi_k + A_n\phi_{k-n\frac{2\pi}{a}} \tag{5.47}$$

This expression is substituted into the Schrödinger equation (5.34) and the resulting equation multiplied on the left by ϕ_k^* or $\phi^*_{k-n\frac{2\pi}{a}}$. On integration, the following simultaneous equations are obtained.

$$A_0[E(k) - E^0(k)] - A_nV_n^* = 0 \tag{5.48}$$

$$-A_0V_n + A_n\left[E(k) - E^0\left(k - n\frac{2\pi}{a}\right)\right] = 0$$

For a non-trivial solution, the determinant of coefficients must vanish. The resulting quadratic has the two solutions

$$E(k) = \tfrac{1}{2}\left[E^0(k) + E^0\left(k - n\frac{2\pi}{a}\right)\right.$$
$$\left. \pm \left[\left(E^0(k) - E^0\left(k - n\frac{2\pi}{a}\right)\right)^2 + 4\mid V_n\mid^2\right]^{\frac{1}{2}}\right] \tag{5.49}$$

At the zone boundary, the two plane wave states have the same energy.

$$\therefore \qquad E^+\left(\frac{n\pi}{a}\right) = E^0\left(\frac{n\pi}{a}\right) + \mid V_n\mid$$

$$E^-\left(\frac{n\pi}{a}\right) = E^0\left(\frac{n\pi}{a}\right) - \mid V_n\mid$$

Near $k = 0$ the difference in unperturbed energies is so large that the perturbation effect is very small. On the other hand, the above analysis shows that there is a discontinuity at the zone boundary and the energy gap is

$$\Delta E = 2\mid V_n\mid$$

Figure 5.9 (a) indicates clearly how the energies are derived

(a) Extended zone scheme $-\infty < k < \infty$

(b) Reduced zone scheme $\frac{-\pi}{a} \leq k \leq \frac{\pi}{a}$
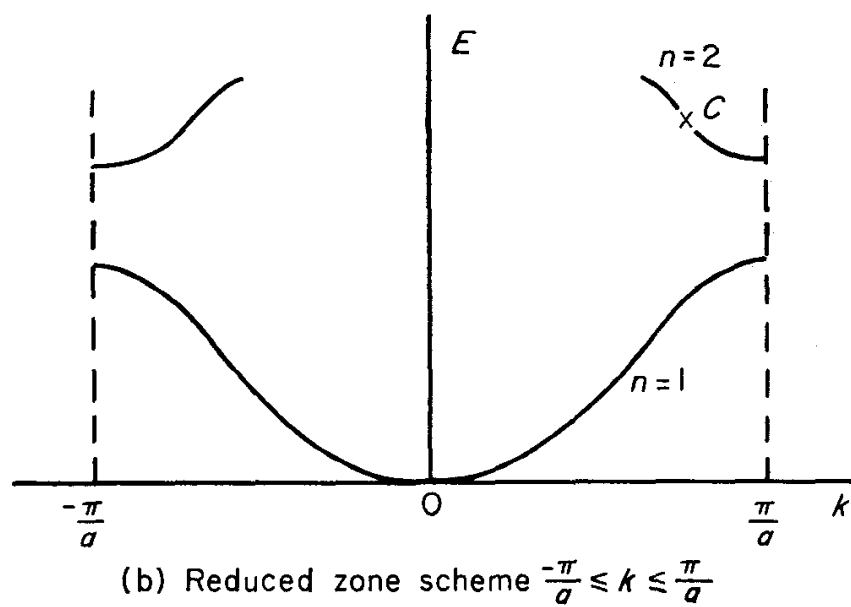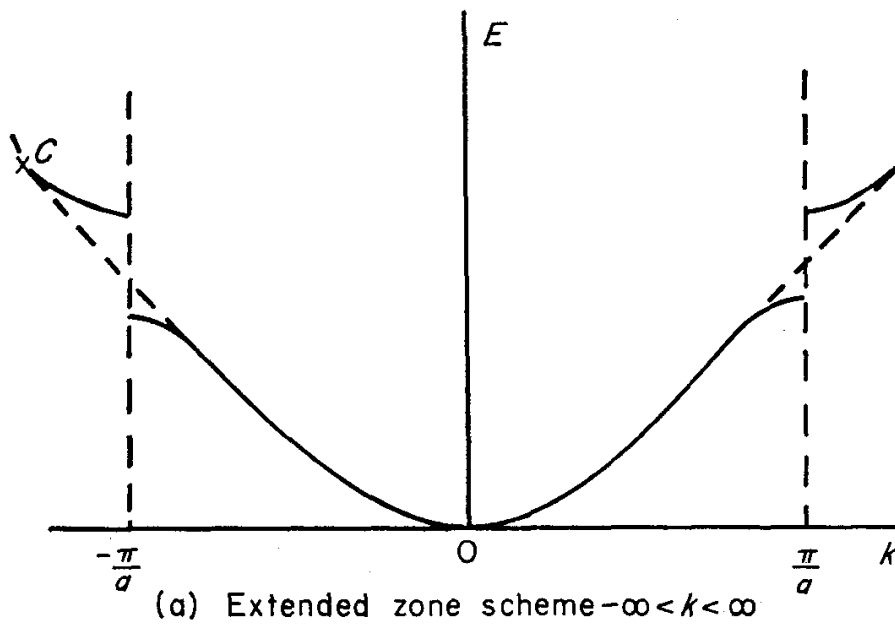
Quantum number n to define band

FIG. 5.9

by perturbation of the free-electron parabola. The two points marked C represent the same state in the two schemes.

For points on either side of the energy discontinuity

$$\left|\frac{A_n}{A_0}\right| = 1 \qquad (5.50)$$

Suppose V_1 is negative. This corresponds to a periodic potential which is negative in the region of each atom ($x = na$) and so attracts electrons. At the zone boundary π/a the wave function belonging to the lower energy E^- is

$$\psi^- = \left(e^{i\frac{\pi}{a}x} + e^{-i\frac{\pi}{a}x}\right)\Big/ \sqrt{\left(2Na\right)}$$

$$= \sqrt{\left(\frac{2}{Na}\right)}\cos\frac{\pi}{a}x$$

Similarly

$$\psi^+ = i\sqrt{\left(\frac{2}{Na}\right)}\sin\frac{\pi}{a}x$$

The lower eiegenfunction has its maximum amplitude at the atom sites where the potential is most attractive. The higher state has its nodes at these points.

If an external electron beam is incident on the crystal with energy lying in one of the gaps it will be totally reflected.

The generalization of this treatment to three-dimensional crystals is straightforward. Energy gaps will occur when

$$E^0(k) = E^0(k - K)$$

with K a reciprocal lattice vector.

i.e. $$|k| = |k - K| \qquad (5.51)$$

Geometrically this means that k lies on the perpendicular bisector of the reciprocal lattice vector K. (This is simply one statement of the Bragg condition.)

So energy gaps occur at the Brillouin zone boundaries and are essentially $2|V_K|$. It is to be expected that at every zone boundary (except for certain symmetry points), there will be a

gap between energy bands. In three-dimensions this does not necessarily imply that there is a forbidden band of energies because the gaps at different parts of the zone occur at different energies so that the bands often overlap.
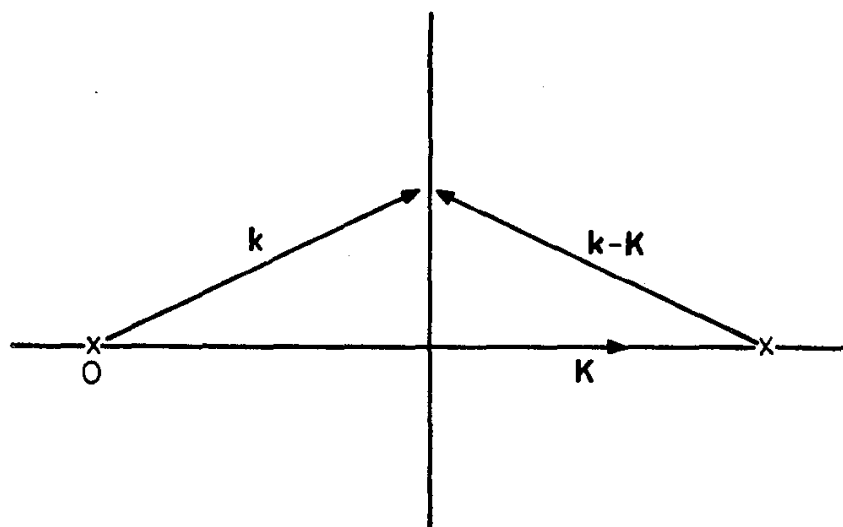
FIG. 5.10

The plane wave approach may be expected to be useful only if the Fourier components V_K converge rapidly. This is certainly not the case. The potential $V(r)$ is due to the periodic array of ions and will have singularities at the ion sites. It has Fourier components of very short wavelength so that V_K may well be considerable for large values of K.

There are several improved methods such as the 'orthogonalized plane wave' technique. (O.P.W. — Herring, 1940) but these are beyond the scope of this monograph.

§ 5.7 Tight-binding model

In the other extreme of tight-binding, it is assumed that the lattice constant is so large that the wave functions of adjacent atoms do not overlap to any appreciable extent. Near the ions cores it is to be expected that the crystal wave function re-

sembles an atomic wave function. In 1928 Bloch pointed out that a crystal wave function with the correct symmetry could be constructed from the atomic orbitals.

$$\psi_k(r) = A(k)\sum_{R_n} e^{ik \cdot R_n} \cdot \phi(r - R_n) \qquad (5.52)$$

where $\phi(r - R_n)$ is an atomic orbital centred on the R_nth site. The constant A is chosen to normalize ψ_k over the microcrystal containing N^3 cells.

The expectation value of the energy for this wave function is

$$E(k) = \frac{\int \psi_k^* \left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(r) \right\} \psi_k \, d\tau}{\int \psi_k^* \psi_k \, d\tau} \qquad (5.53)$$

$$\therefore \qquad E(k) = A^2 N^3 \sum_{R_l} e^{-ik \cdot R_l} \epsilon(R_l) \qquad (5.54)$$

with $\quad \epsilon(R_l) = \int \phi^*(r - R_l)\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V \right\}\phi(r) \, d\tau \quad (5.55)$

Equation (5.54) expresses the periodicity of the energy function in k-space and the Fourier coefficient $\epsilon(R_l)$ is the matrix element of the Hamiltonian between the atomic orbitals on sites separated by R_l. These Fourier coefficients involve three centre
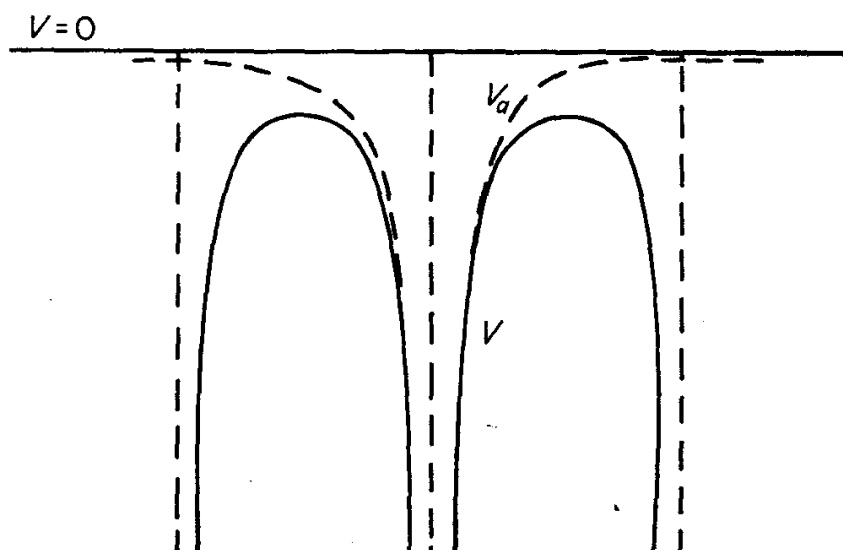
Fig. 5.11   Atomic and crystal potentials

integrals as the crystal potential is normally expressed as a superposition of atomic potentials.

A simplified treatment is given below. The atomic functions satisfy the Hamiltonian for a free atom.

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_a(r)\right\}\phi = E_a\phi \qquad (5.56)$$

$$\therefore \qquad \left\{-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right\}\phi = [E_a + (V(r) - V_a(r))]\phi$$

V_a is the potential for a free atom and E_a is an eigenvalue. If the overlap between different atomic functions is neglected $A^2 = 1/N^3$ and

$$\epsilon(0) = E_a + \alpha \qquad (5.57)$$

with $$\alpha = \int \phi^*[V - V_a]\phi \, d\tau$$

$$\epsilon(R_l) = \int \phi^*(r - R_l)[V - V_a]\phi(r) \, d\tau \qquad (5.58)$$

In fact, some overlap between $\phi(r - R_l)$ and $\phi(r)$ is assumed so that $\epsilon(R_l)$ is not zero but $\epsilon(R_l)$ will certainly be very small except for nearest neighbours. If the atomic wave functions have spherical symmetry, the integral (5.58) will be the same for all the nearest neighbours.

i.e. $$\epsilon(R_l) = \beta \qquad \text{for nearest neighbours} \qquad (5.59)$$

In this nearest-neighbour interaction approximation the energy is

$$E(k) = E_a + \alpha + \beta\sum_{R_n} e^{-ik \cdot R} \qquad (5.60)$$

As $(V - V_a)$ is negative, the integrals α, β are both negative and may be of the order of a few electron volts.

For a simple cubic lattice, there are six nearest neighbours at the sites $(a, 0, 0)$, etc.

$$E(k) = E_a + \alpha + 2\beta[\cos ak_x + \cos ak_y + \cos ak_z] \qquad (5.61)$$

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(a) Brillouin zone

(b) Energy plot along section AB
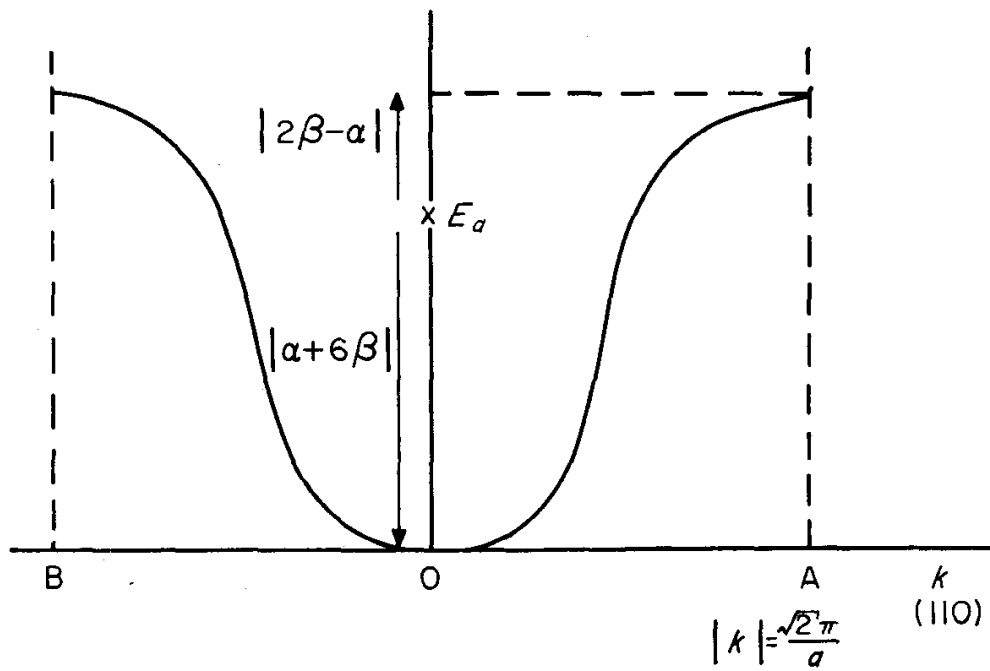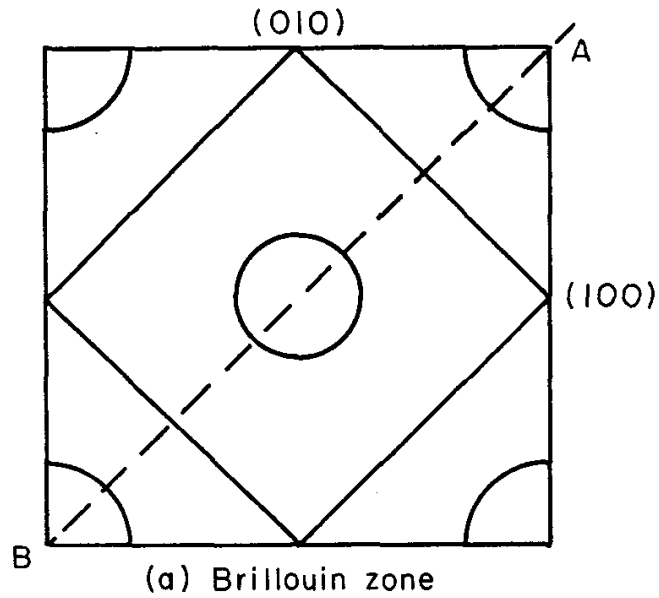
FIG. 5.12 Simple cubic lattice

The Brillouin zone is a cube and Fig. 5.12 illustrates the energy contours in the k_x, k_y plane.

The band has a width $12 \mid \beta \mid$.

Each atomic level in the free atom will split into a band of energies as the atoms are brought together to form a crystal. The N^3 atoms originally contain N^3 degenerate levels. The final band contains N^3 different levels. The integral β and hence the width of the band depends upon the overlap of the atomic wave functions. The band will tend to be very narrow if the atomic orbitals are closely localized. In practice, the band widths of inner core electrons are vanishingly small.

If two atomic levels broaden so much that they almost intersect, then it is clear that the method described above may not be sufficient. If $E_b - E_a$, the separation between two atomic levels, is of the same order or less than the band width 12β it is
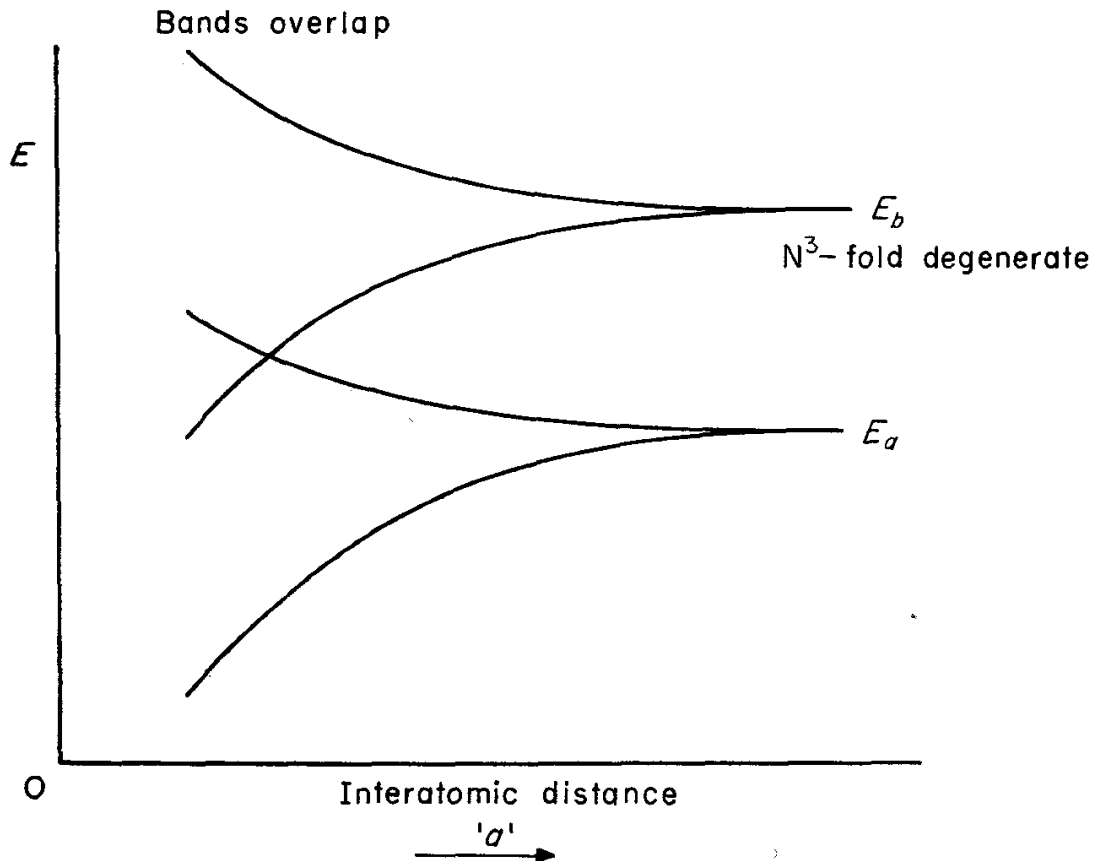
FIG. 5.13

necessary to assume that the wave function is a linear combination of atomic orbitals (L.C.A.O.).

$$\psi_k(r) = \sum_j A_j(k) \sum_{R_n} e^{ik \cdot R_n} \phi_j(r - R_n) \qquad (5.62)$$

The sum over j includes all the atomic wave functions considered necessary. For example, a triple degenerate p-state in an atom is split into three energy bands degenerate at the centre of the Brillouin zone at $k = 0$. The j-sum in (5.62) must include all three p-functions. If an s-state occurs close to a triply degenerate p-state, as in carbon, then the L.C.A.O. method involves a sum over all four atomic orbitals. In general, the more atomic functions in the sum, the more accurate the final energy band will be. The expression (5.62) is used as a trial wave function and the energy is minimized. This will result in a set of linear equations, the number being equal to the number of atomic orbitals and the coefficients A_j are the solutions.

The L.C.A.O. method has certain disadvantages. The bound states of an atom do not form a complete set of functions as the ionized plane wave states are not included. The overlap integrals between atomic orbitals on different sites are not negligible and this complicates the algebra. Slater and Koster (1954) have used the L.C.A.O. method in an interpolation scheme, fitting the interaction integrals (5.55) to values either observed empirically or calculated from the results of other methods.

§ 5.8 The Wannier function

The atomic orbitals used in the L.C.A.O. method are not orthogonal and calculations involving them are often tedious. Wannier (1937) introduced a set of orthogonal localized functions which may be used to describe a band. The Wannier function is defined by a sum over the Brillouin zone of the Bloch functions for the band.

$$a(r - R_n) = \frac{1}{\sqrt{N^3}} \sum_k e^{-ik \cdot R_n} \psi_k(r) \qquad (5.63)$$

$a(\boldsymbol{r} - \boldsymbol{R}_n)$ denotes the Wannier function on the $\boldsymbol{R}_n$th site. It is a trivial matter to demonstrate that the N^3 Wannier functions centred on different sites are orthogonal. Similarly, the Wannier functions belonging to different bands i and j are also orthogonal.

$$\int a_i{}^*(\boldsymbol{r} - \boldsymbol{R}_n)a_j(\boldsymbol{r} - \boldsymbol{R}_m) \, \mathrm{d}\tau$$

$$= \frac{1}{N^3}\sum_k\sum_{k'}e^{ik.R_n}e^{-ik'.R_m}\int\psi_{ik}{}^*(\boldsymbol{r})\psi_{jk'}(\boldsymbol{r}) \, \mathrm{d}\tau$$

$$= \frac{1}{N^3}\sum_k\sum_{k'}e^{ik.R_n}e^{-ik'.R_m}\delta_{ij}\delta_{kk'}$$

$$= \delta_{ij}\delta_{nm}$$

as $$\sum_k e^{ik.(R_n - R_m)} = N^3\delta_{nm}$$

If equation (5.63) is multiplied by $e^{ik'.R_n}$ and summed over $\boldsymbol{R}_n$ then from the result

$$\sum_{R_n} e^{i(k - k')R_n} = N^3\delta_{kk'}$$

it is simple to verify

$$\psi_{k'}(\boldsymbol{r}) = \frac{1}{\sqrt{N^3}}\sum_{R_n}e^{ik'.R_n}a(\boldsymbol{r} - \boldsymbol{R}_n) \qquad (5.64)$$

The Wannier functions may be considered as the Fourier components of all the Bloch functions belonging to a band. The Wannier functions centred on different sites are all identical. From (5.63)

$$\{\epsilon \mid -\boldsymbol{R}_n\}a(\boldsymbol{r} - \boldsymbol{R}_n) = \frac{1}{\sqrt{N^3}}\sum_k e^{-ik.R_n}e^{ik.R_n}\psi_k(\boldsymbol{r}) = a(\boldsymbol{r})$$

The usefulness of the Wannier function arises because it is localized

$$a(\boldsymbol{r} - \boldsymbol{R}_n) = \frac{1}{\sqrt{N^3}}\sum_k e^{ik(r - R_n)}u_k(\boldsymbol{r})$$

Except where $\boldsymbol{r} - \boldsymbol{R}_n$ is small, the exponential term is rapidly varying in $\boldsymbol{k}$-space and the summation is small. The Wannier

function on the nth site has an appreciable value only in the vicinity of the site. Blount (1962) showed that for bands which do not have degeneracies the Wannier function may be chosen to fall off faster than any finite power of r. Where there is a point degeneracy the Wannier function may decay as r^{-3} and for a line degeneracy it may decay as r^{-2}.

The Bloch waves satisfy the Schrödinger equation

$$\mathscr{H}\psi_k = E(k)\psi_k$$

The energy is periodic in k-space and can be expressed as a Fourier expansion

$$E(k) = \sum_{R_m} e^{-ik \cdot R_m} \epsilon(R_m) \qquad (5.65)$$

If (5.64) and (5.65) are used to substitute for ψ_k and $E(k)$ in the Schrödinger equation then

$$\sum_{R_n} e^{ik \cdot R_n}\mathscr{H}a(r - R_n) = \sum_{R_l}\sum_{R_m} \epsilon(R_m)e^{ik \cdot (R_l - R_m)}a(r - R_l)$$

This equation may be multiplied on the left by $e^{-ik \cdot R_j}$ and summed over k. It follows that

$$\mathscr{H}a(r - R_j) = \sum_{R_i}\epsilon(R_i)a(r - R_i - R_j) \qquad (5.66)$$

The Wannier functions satisfy a non-diagonal form of the Hartree–Fock equations.

There is an intrinsic ambiguity in the Wannier function definition (5.63). The Bloch waves as solutions of Schrödinger's equation are only defined to within an arbitrary phase factor $e^{i\phi}$. However, it can be shown that the phase can always be chosen so that

$$\psi_k{}^* = \psi_{-k}$$

In this case

$$a^*(r) = \frac{1}{\sqrt{N^3}}\sum_k \psi_k{}^* = \frac{1}{\sqrt{N^3}}\sum_k \psi_{-k} = a(r)$$

The Wannier function may always be chosen to be real and for a non-degenerate band this function decays exponentially.

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Wannier functions have proved themselves useful in the study of impurities in crystals, but in general it is difficult to find the Wannier function as it is necessary to know all the Bloch waves in a band. However, if the Bloch functions are given by the tight-binding approximation the Wannier function is easily found. Consider a one-dimensional lattice of like atoms with one electron per atom. The Bloch wave is

$$\psi_k(x) = A(k)\sum_n e^{ikna}\phi(x - na)$$

where $\phi(x - na)$ is the atomic-orbital on the nth atom and $A(k)$ is a constant normalizing the Bloch function over N cells. If the atomic orbitals are orthogonal $A = 1/\sqrt{N}$ and the approximate Wannier function is simply the atomic orbital. More generally

$$A(k) = [N(\sum_n e^{ikna}S(0, n))]^{-\frac{1}{2}}$$

with
$$S(m, n) = \int \phi^*(x - ma)\phi(x - na)\,dx$$

The Wannier function at the origin is

$$a(x) = \frac{1}{\sqrt{N}}\sum_k \psi_k(x)$$

i.e.
$$a(x) = \frac{1}{N}\sum_k \left[\sum_m e^{ikma}S(0, m)\right]^{-\frac{1}{2}}\sum_n e^{ikna}\phi(x - na)$$

If the overlap integrals are small and satisfy

$$\sum_{m \neq 0} S(0, m) < 1$$

then
$$(\sum_m e^{ikma}S(0, m))^{-\frac{1}{2}} = 1 - \tfrac{1}{2}\sum_{m \neq 0} e^{ikma}S(0, m) + \ldots$$

To this approximation the Wannier function is

$$a(x) = \phi(x) - \tfrac{1}{2}\sum_{n \neq 0} S(0, n)\phi(x + na) \qquad \cdot$$

§ 5.9 The cellular method

This method was first used by Wigner and Seitz (1933, 1934). The cellular method is a completely different approach to the band problem than either the plane-wave method or the tight-binding approximation. In the latter methods, the wave functions are chosen from the start to be Bloch functions satisfying the conditions imposed by the lattice periodicity, and then the ionic potential is considered as a perturbation. The cellular method, on the other hand, attempts to find as exact a solution as possible near the ion cores and then to approximate to the boundary conditions. A more complete discussion will be given in Chapter 7.

§ 5.10 Motion in steady fields

In general each Bloch wave is complex and describes a state with definite mean velocity. Formally the velocity is (in the absence of a vector potential)

$$V(k) = \frac{\hbar}{2mi} \int [\psi_k{}^* \ \mathrm{grad} \ \psi_k - \psi_k \ \mathrm{grad} \ \psi_k{}^*] \ \mathrm{d}\tau$$

The integral on the r.h.s. may be evaluated to give

$$V(k) = \frac{1}{\hbar} \ \mathrm{grad}_k E(k) \tag{5.67}$$

$E(k)$ is the band energy function. This equation refers to a single Bloch state but a simplified wave-packet argument gives the same result. The complete time-dependent wave function for a Bloch state is

$$\psi_k(r, t) = u_k(r) e^{i\left[k \cdot r - \frac{Et}{\hbar}\right]} \tag{5.68}$$

A wave packet with peak at k_0 may be constructed from Bloch functions belonging to a given band

$$\psi(r, t) = \int_{B.Z.} a(k) \psi_k(r, t) \ \mathrm{d}k \tag{5.69}$$

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The integral is over the Brillouin zone. If the packet is sufficiently concentrated so that $E(k)$ may be replaced by its Taylor expansion to terms linear in k then

$$E(k) = E(k_0) + \text{grad}_k E(k_0) \cdot (k - k_0)$$

and

$$\psi(r, t) = e^i\left[k_0 \cdot r - \frac{E(k_0)t}{\hbar}\right] \cdot \int_{B.Z.} a(k) u_k e^{i(k - k_0)}\left[r - \frac{t}{\hbar}\text{grad}_k E(k)\right] dk$$

The probability density $\psi^*\psi$ depends only on the integral and so will essentially remain constant along a trajectory for which

$$r = \frac{t}{\hbar}\text{grad}_k E$$

The velocity of the wave packet is

$$V(k) = \frac{1}{\hbar}\text{grad}_k E \tag{5.70}$$

When a static electric field is applied to the crystal, the electrons will be accelerated and gain kinetic energy. Of course, total energy remains constant and stationary states do exist. The study of the electronic motion in a steady uniform field is surprisingly quite complicated. The Schrödinger equation now includes an extra potential

$$U = e\mathscr{E} \cdot r \tag{5.71}$$

$\mathscr{E}$ is the electric field strength and $-e$ the electron charge. Ordinary perturbation theory cannot be used to solve this problem as the extra potential becomes arbitrarily large for sufficiently large distances.

Free electrons would be accelerated off to infinity by an electric field. In one-dimension, the operator which has eigenvalues $\hbar k$ is just the linear momentum operator $\hat{p} \equiv \frac{\hbar}{i}\frac{\partial}{\partial x}$ (see (5.35)). (This is not the case in crystals.) If the wave function ψ represents a wave packet with mean momentum $\hbar k$, then the rate of change of this momentum is

$$\hbar k = \frac{i}{\hbar} \int \psi^* (\mathscr{H} \hat{p} - \hat{p} \mathscr{H}) \psi \, d\tau \qquad (5.72)$$

$$\mathscr{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + e\mathscr{E} x$$

The field $\mathscr{E}$ is in the positive x-direction. Equation (5.72) becomes

$$\hbar \dot{k} = -e\mathscr{E} \qquad (5.73)$$

This final result is an expression of Newton's second law — the applied force is proportional to the rate of change of linear momentum.

Equation (5.73) is also true for electrons in crystals, but this does require some amplification. In crystals, k defines a Bloch wave, that is a function which is an eigenfunction of both the Hamiltonian and translation operators. But the new term $e\mathscr{E} . r$ does not have the lattice periodicity and k is no longer a constant of the motion. The effect of the field is to induce transitions from one energy state to another. For weak fields $(<10^6 Vm^{-1})$ band transitions are improbable and so the main effect is to alter k. If k is the mean wave vector of a wave packet constructed from a single band, the change in band energy of the 'electron' in unit time is

$$\text{grad}_k E . \dot{k}$$

The work done on the electron by the field in this time is

$$-e\mathscr{E} V(k) = -\frac{e}{\hbar} \text{grad}_k E . \mathscr{E}$$

These expressions must be equal and

$$\hbar \dot{k} = -e\mathscr{E} \qquad (5.74)$$

is a solution.

For the mean k-vector of a packet to have significance it is necessary that the packet be spread over several crystal primitive cells in real space. Consequently the argument is only valid in general if the field is sufficiently slow-varying. A more formal

proof would take account of inter-band transitions (Zener effect).

This result is not quite so obvious as the corresponding free electron case. Here $\hbar k$ does not represent the real momentum but the 'crystal momentum', and will be considered further in the next section. Equation (5.74) is a modified Newton's law for Bloch wave packets — the external force is equal to the rate of change of crystal momentum.

In the presence of a combined electric-magnetic field the appropriate result is

$$\hbar \dot{k} = -e[\mathscr{E} + V \wedge B] \qquad (5.75)$$

B is the magnetic flux vector.

For a magnetic field alone it would seem reasonable to write

$$\hbar \dot{k} = -eV \wedge B \qquad (5.76)$$

This cannot be proved in the same way, as the force is always perpendicular to the velocity and the work done by the field is zero. Even so, the formula is correct up to a point, but it does neglect the fact that in a magnetic field the electron describes closed orbits and a set of discrete energy levels is formed.

§ 5.11 The crystal momentum

The solution of Schrödinger's equation for a free-particle is $Ae^{ik \cdot r}$ (A is a normalizing constant). This wave function is also an eigenfunction of the momentum operator $\dfrac{\hbar}{i}$ grad with momentum eigenvalue $\hbar k$.

By analogy the quantity $\hbar k$ where k defines a Bloch wave, is called the crystal momentum. This is not the true momentum of the electron. Linear momentum is not conserved in a periodic field.

The expectation value of the real momentum of a Bloch state is

$$\bar{p} = \int \psi_k^* \frac{\hbar}{i} \operatorname{grad} \psi_k \, d\tau \qquad (5.77)$$

The periodic part of the Bloch wave may be expanded in a Fourier series (plane wave expansion).

$$\psi_k(r) = \frac{1}{\sqrt{\Omega}} \sum_{K_m} e^{i(k+K_m)\cdot r} W(k + K_m) \qquad (5.78)$$

From (5.77) and (5.78)

$$\bar{p} = \sum_{K_m} | W(k + K_m) |^2 \hbar(k + K_m) \qquad (5.79)$$

The real momentum may take the values $\hbar(k + K_m)$ with the respective probabilities $| W(k + K_m) |^2$.

Equation (5.75) illustrates one aspect of how the crystal momentum replaces linear momentum in crystals. Another is obtained by considering a collision between two Bloch electrons. For classical particles, linear momentum is conserved in a collision. An analogous result holds true for electrons in crystals.

A system of two electrons in a periodic field is described by a two-electron wave function. The two-electron Schrödinger equation must be invariant under a lattice translation and so

$$\{\epsilon \mid R_n\}\psi(r_1, r_2) = e^{-ik\cdot R_n}\psi(r_1, r_2) \qquad (5.80)$$

The wave function may be characterized by the vector k and $\hbar k$ is the crystal momentum for the two electrons. When the two electrons are sufficiently far apart for their interaction to be negligible, the wave function is the product of the one-electron Bloch waves with wave vectors k_1 and k_2 respectively.

$$\psi(r_1, r_2) = \phi_{k_1}(r_1)\phi_{k_2}(r_2)$$

Clearly

$$\{\epsilon \mid R_n\}\phi_{k_1}\phi_{k_2} = e^{-iR_n\cdot(k_1+k_2)}\phi_{k_1}\phi_{k_2} \qquad (5.81)$$

Comparing (5.80) and (5.81)

$$k = k_1 + k_2 + K \qquad (5.82)$$

The crystal momentum of the system is equal to the sum of the momentum of the electrons, apart from an arbitrary reciprocal lattice vector. As k is a constant of the motion it follows that if

the two electrons collide, the sum of their crystal momenta before is equal to the sum of the momenta after, apart from a reciprocal lattice vector.

i.e. $$k_1 + k_2 = k_1' + k_2' + K \qquad (5.83)$$

§ 5.12 The electric current

Each Bloch wave represents a moving charge with a mean velocity $V(k)$ (5.67). The total current carried by a full band is clearly proportional to the integral

$$-e\int_{B.Z.} f(k)V(k)\,\mathrm{d}k \qquad (5.84)$$

where $f(k)$ is the probability that the state k is occupied. In equilibrium this is the Fermi–Dirac function. For a full band $f(k) = 1$ for all k. (Each k-state contains two electrons.) As energy bands always have inversion symmetry $V(k) = -V(-k)$ and the current integral (5.84) is zero.

To produce a current, an electric field must excite some electrons into states representing a net current. If there is an energy gap between a filled valence band and an empty 'conduction' band, a finite excitation energy is required to lift the electron into the next band. Normally this cannot be supplied by a constant electric field and the solid will be an insulator. If the energy gap is small then at temperatures above absolute zero there will be a small but not zero number of electrons excited in to the upper band and a corresponding number of 'holes' in the lower band. These electrons will be able to carry a current and the conductivity will increase with temperature. Such substances are semiconductors. If the band is not full then although the true ground state will represent a state with zero current, electrons are easily excited into the infinitesimally higher energy states. The conductivity is high and may be expected to decrease with temperature as the scattering pro-
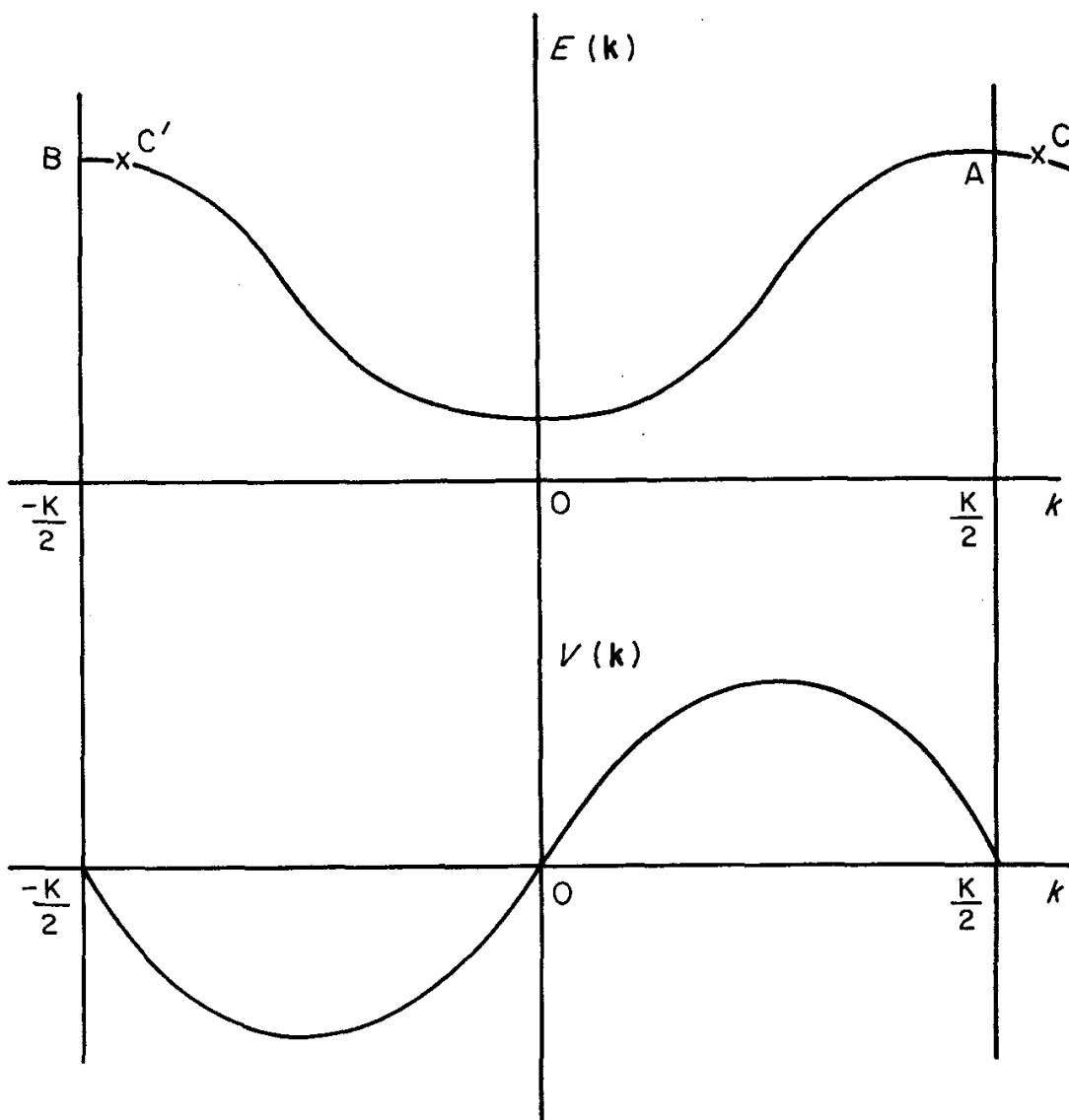
FIG. 5.14   A band has inversion symmetry

cesses become more effective. These substances are conductors.

A Brillouin zone contains exactly as many allowed k-states as there are primitive cells in the micro-crystal. Each state may contain up to two electrons of opposite spin and if the crystal contains N^3 cells then each energy band may contain up to $2N^3$ electrons.

Typical metals are the alkalis Li, Na, K, Rb, Cs and the noble metals Cu, Ag, Au. Each primitive cell contains one

atom and hence contributes one free-electron. There are N^3 electrons for $2N^3$ places and so all these metals have a half-filled energy band. If the solid has an odd number of available electrons per cell it is always a metal. Insulators may arise when

TABLE 5.1

	Metal	Semiconductor	Insulator
Substance	Copper	Silicon	Diamond
Resistivity Ohm cm	$3 \cdot 6 \cdot 10^{-6}$	$\sim 2 \cdot 10^5$	$10^{12} \sim 10^{13}$

there is an even number of electrons per cell (e.g. diamond has eight). This is not necessarily so as bands may overlap in energy and parts of a lower band may be unfilled and some electrons
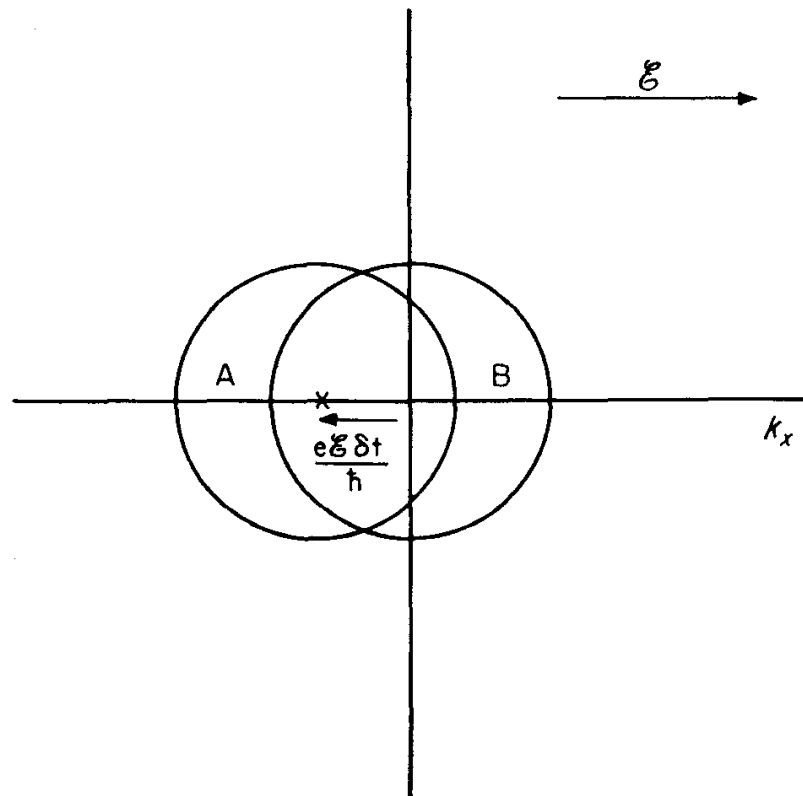
FIG. 5.15   Movement of Fermi surface in a field

may be in the upper band. In fact the divalent elements are metals because of this reason.

The movement of a Fermi surface in a conductor is worthy of mention. In a zero field, the electrons are in an equilibrium distribution filling k-space up to a Fermi energy or if the temperature is above absolute zero, the occupation will decrease rapidly near the Fermi energy. Immediately the electric field is applied the electron states begin to move in k-space with a velocity given by (5.74). The electron distribution will move bodily in the direction opposed to the field and in a time δt the centre will move a distance $-e\mathscr{E}\,\delta t/\hbar$. Some of the electrons increase their band energies $E(k)$, others show a decrease.

In a perfect crystal this process would continue indefinitely. A given state k would move towards the edge of the zone and then re-appear at the opposite side (C, C' represent the same state, Fig. 5.14), and the state would continuously traverse the band in a direction opposed to the field. In real space the electron would oscillate both with and against the field (the velocity is zero at A, B, Fig. 5.14), undergoing a Bragg reflection at the zone edge. The time for one complete cycle is the time T for k to change from $-K/2$ to $K/2$. If K is taken to be $2\pi/a$ where a is the separation between atom planes perpendicular to the field, then

$$T = h/e\mathscr{E}a \qquad (5.85)$$

For normal fields $\mathscr{E} \sim 10^6 Vm^{-1}$, $T \sim 10^{-9}$ sec.

If this oscillation took place in conductors then no net current would be carried.

As conductors do allow current flow, then clearly there must be some other factor not yet taken into account. The process ignored up to this point has been the electron scattering due to the deviations of the crystal from true periodicity. In a real crystal, electrons in the 'high energy' region A (Fig. 5.15), undergo transitions to B. These transitions, which normally do not involve appreciable loss in electron energy, are brought

about by the thermal vibrations of the lattice and by impurities. A state of dynamic equilibrium is set up and if τ is the average lifetime in the region A above the Fermi-energy before scattering takes place, the centre of the electron distribution will move a distance $e\mathscr{E}\tau/\hbar$ in k-space. The mean shift in the distribution represents a drift velocity superimposed upon the random electron motion, i.e. a current.

In metals $\tau \sim 10^{-12}$ secs (at room temperature) and so the oscillations described previously do not take place. On the other hand, scattering does not take place in insulators as there are no final empty states, and so the electrons may be considered to carry out the oscillations.

This periodic wave-packet motion is quantized and the energy levels can be shown to be $e\mathscr{E}a$ apart. This system of discrete levels forms a 'Stark ladder'. For normal fields the splitting is extremely small $\sim 10^{-6}$eV but it has been observed in p-n junctions where the local field may be $\sim 10^{10}$Vm^{-1}. For further information the reader is referred to the literature (Wannier, 1962).

§ 5.13 The Zener effect

The most important effect of a weak uniform electric field is to accelerate the electrons and their motions in k-space are given by equation (5.74). In this simplified theory the electron oscillates back and forth in a bounded state. (In a perfect crystal.) But bounded states do not really exist in an electric field. Consider the potential energy diagram (Fig. 5.16), which shows the effect of an electric field on a one-dimensional potential well. When there is no applied field, the state with energy E is bound, but when the field $\mathscr{E}$ is applied as shown there is a finite possibility for the electron to tunnel to the left. For weak fields, the likelihood of tunnelling is very small and so the lifetime of the bound state is correspondingly large.

Tunnelling is the basis of the Zener effect. The band structure

$$V = -W \quad -a < x < a$$
$$V = 0 \qquad |x| > a$$

$$V = -W + e\mathscr{E}\, x \quad -a < x < a$$
$$V = e\mathscr{E}\, x \qquad |x| > a$$

Fig. 5.16

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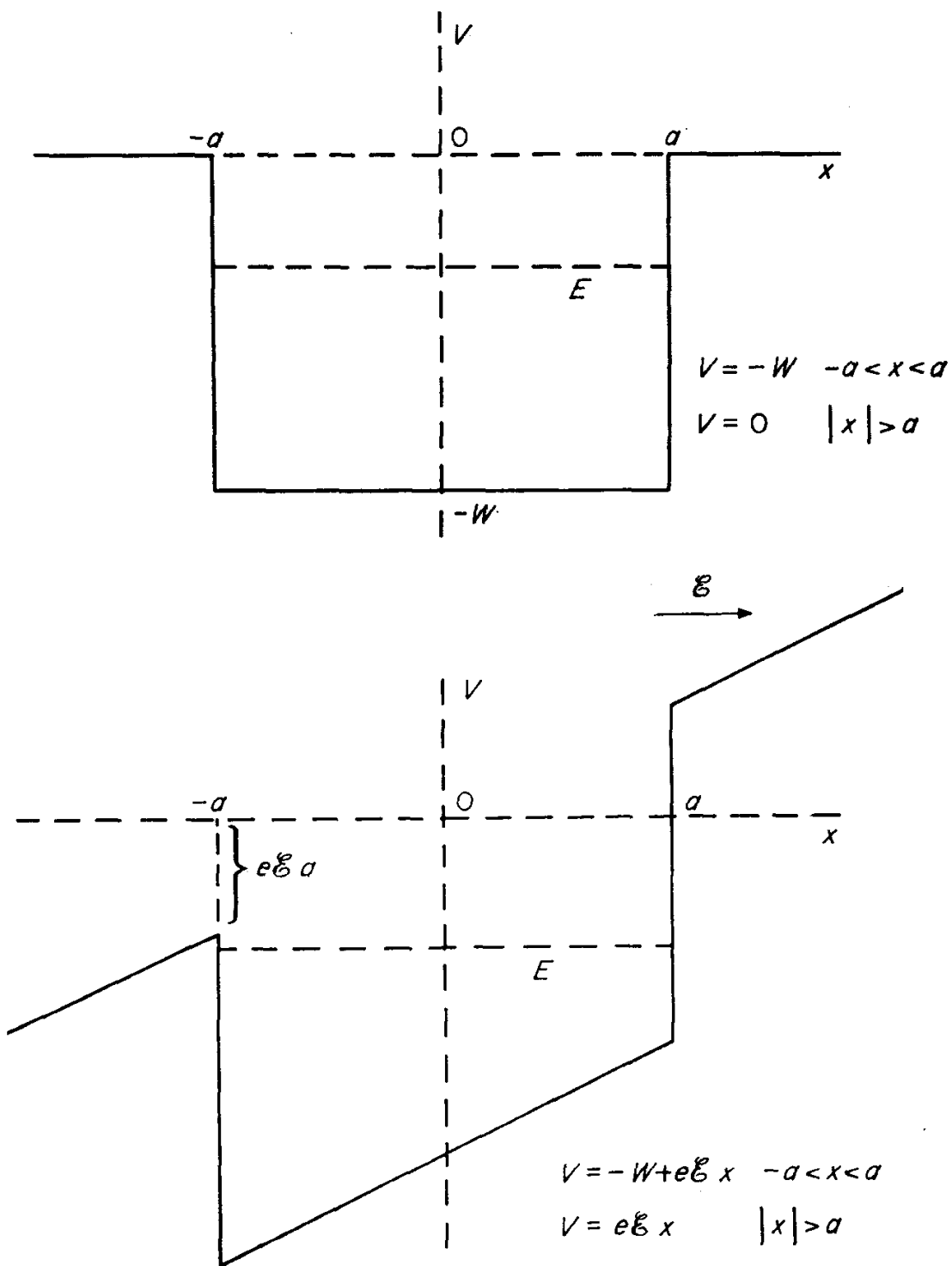
in the presence of an electric field is illustrated in Fig. 5.17. The potential energy at the base of the conduction band has a slope $e\mathscr{E}$. The relative positions of the other band edges are not altered by the field. As k varies, an electron in the valence band oscillates between A and B and the total energy remains con-
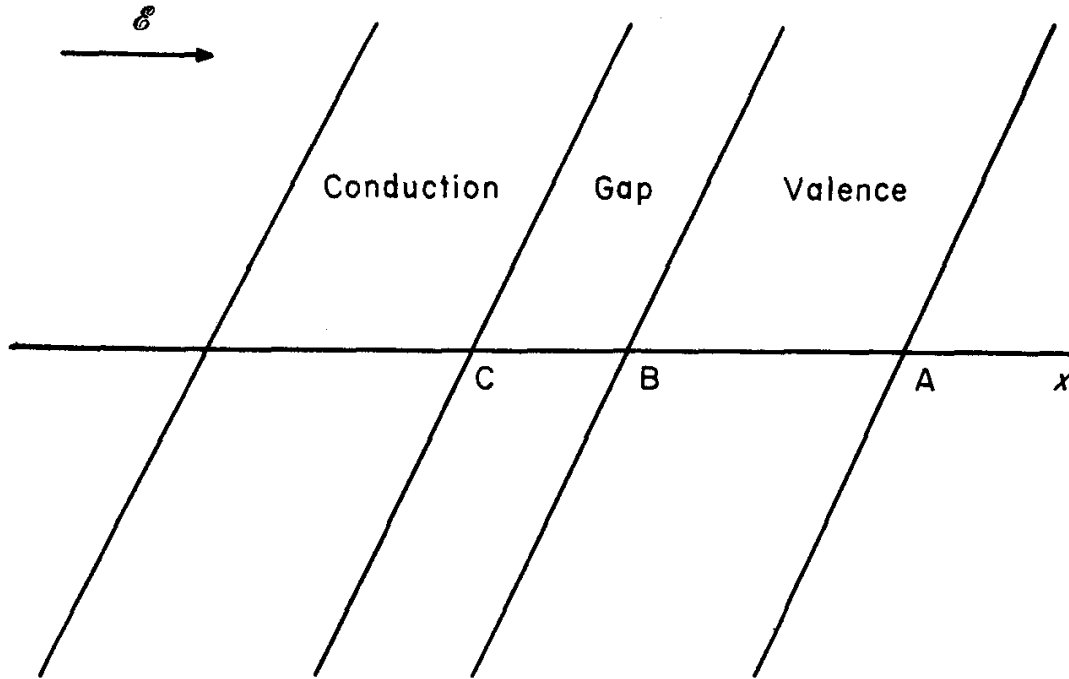
FIG. 5.17   Band structure in an applied field

stant. Now, however, there is a small but definite possibility that the electron will tunnel the forbidden gap to C in the conduction band. No change of total energy is involved.

It can be shown that for the probability for such a transition to be appreciable, the field must be of the order of $10^9 Vm^{-1}$. This is one theory of breakdown in insulators, but it is probable that other causes are more important.

A true Zener effect has been observed at p–n junctions in semiconductors.

§ 5.14 The effective mass-holes

In many respects the motion of an electron wave packet in a crystal is related to that of a free-electron. In particular, the velocity remains a constant when there is no external applied force. Near the top or bottom of a band it is often possible to extend this correspondence by introducing the concept of 'effective mass'. This is particularly useful when studying the properties of the charge carriers in semiconductors.

In the vicinity of an energy minimum or maximum, if there are no degeneracies, the function $E(k)$ is analytic and may be expanded in a power series with no linear terms. Let k_0 be a stationary point.

$$E(k) = E(k_0) + \tfrac{1}{2}\sum_i\sum_j\alpha_{ij}(k_i - k_{0i})(k_j - k_{0j}) + \ldots$$

By a suitable rotation of the co-ordinates the cross-terms may be removed.

$$E(k') = E(k_0) + \frac{\hbar^2}{2}\left(\frac{k_1'^2}{m_1{}^*} + \frac{k_2'^2}{m_2{}^*} + \frac{k_3'^2}{m_3{}^*}\right) + \ldots \quad (5.86)$$

The orthogonal co-ordinates k_i' are linear combinations of the co-ordinates $(k_i - k_{0i})$ and

$$m_i{}^* = \hbar^2 \bigg/ \left(\frac{\partial^2 E}{\partial k_i'^2}\right)_{k_0} \quad (5.87)$$

Compare equation (5.61) for the simple cubic structure. For small k

$$E(k) = (E_a + \alpha + 6\beta) - \beta a^2(k_x^2 + k_y^2 + k_z^2)$$

and

$$m^* = -\hbar^2/2\beta a^2$$

If there is a minimum at k_0 the constants $m_i{}^*$ are all positive. Equation (5.70) is still valid in the new co-ordinates and

$$V_i(k') = \frac{\hbar k_i'}{m_i{}^*} \quad (5.88)$$

The acceleration of the state in a field is from (5.74)

$$m_i^* \dot{V}_i(\mathbf{k}') = -e\mathscr{E}_i \qquad i = 1, 2, 3 \qquad (5.89)$$

This final equation is analogous to Newton's law. The motion of the state is classical except that three different masses m_i^* are used for the three directions. This effective mass description is well suited for discussing the properties of those excited electrons in a semiconductor which are near the energy minimum in the conduction band.

At the top of a band, equation (5.86) will again be correct, but in this case the three masses m_i^* must be negative. It is often convenient to redefine the masses to be positive and then

$$E(\mathbf{k}') = E(\mathbf{k}_0) - \frac{\hbar^2}{2}\left(\frac{k_1'^2}{m_1^*} + \frac{k_2'^2}{m_2^*} + \frac{k_3'^2}{m_3^*}\right) \qquad (5.90)$$

$$m_i^* = -\hbar^2\Big/\left(\frac{\partial^2 E}{\partial k_i'^2}\right)_{k_0}$$

The equations analogous to (5.89) are

$$m_i^* \dot{V}_i(\mathbf{k}') = e\mathscr{E}_i \qquad (5.91)$$

A state near the top of a band behaves as a particle with either positive masses m_i^* and positive charge or negative masses and negative charge.

The former interpretation is usual for semiconductors. At the top of the valence band there are unoccupied electron states or holes. Instead of studying the nearly full band in terms of the many occupied states it is simpler to give a description in terms of the holes. A little thought should convince the reader that a hole will travel through space at the same rate as its neighbours and so the velocity of a hole is the same as that of an electron in that state. A full band carries no current at all and so a band with one electron missing must carry the negative current which that electron would carry. Clearly if the hole description is to be used then a hole must produce the same current as a positive electron in the same state. So, in semiconductor theory, a nearly full valence band is conveniently described by a few

positive charge carriers with positive masses and the current carried by the band is proportional to the integral

$$+ e\int_{B.Z.} [1 - f(k)]\, V(k)\; dk$$
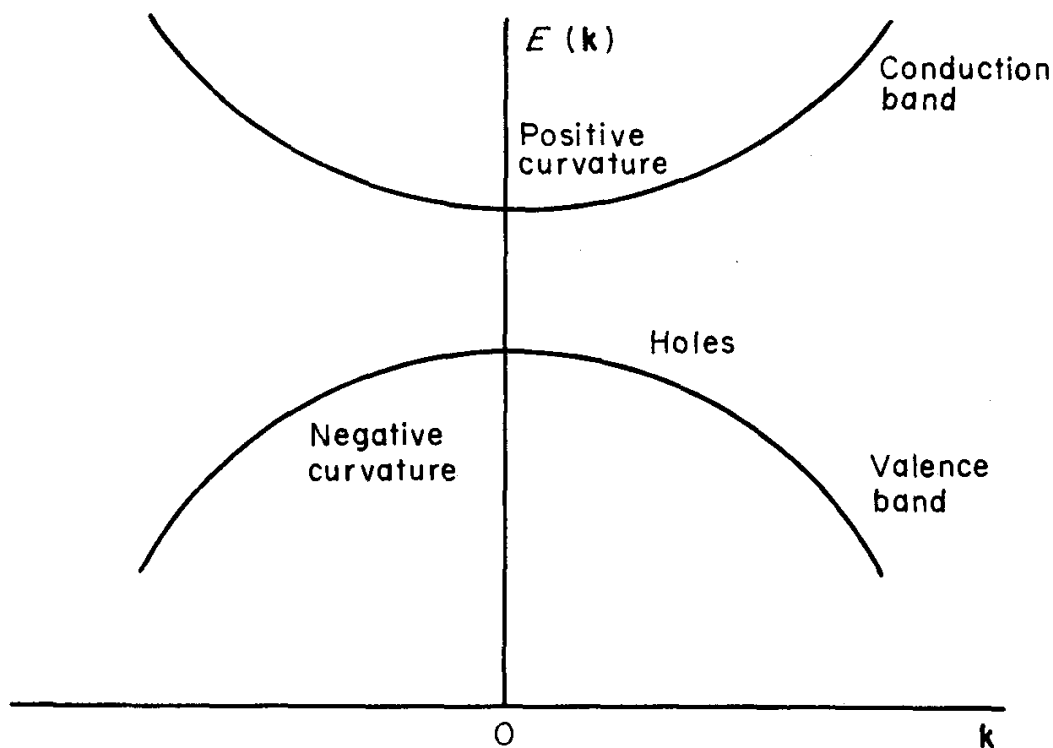
FIG. 5.18

§ 5.15 Cyclotron resonance

The experimental study of the motion of crystal electrons in a magnetic field has proved to be a most fruitful source of information about the band structure.

When a steady uniform magnetic field is applied to the crystal an electron state moves in k-space so that the vector k is perpendicular to both the applied field and the velocity.

$$\hbar \dot{k} = -e V \wedge B \qquad (5.92)$$

A wave packet in k-space does not gain kinetic energy from a magnetic field and so the 'orbits' are the intersections of the

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constant energy surface in k-space with planes perpendicular to the field. The component of k parallel to B remains constant at its initial value. In real space the electrons move in helices. (In fact the orbit will only be a true helix if the energy surfaces are axially symmetric about the field B.)

The frequency of rotation of the electrons depends upon the magnitude of the field and the structure of the energy bands. Consider two neighbouring energy contours in k-space in a plane perpendicular to the field.
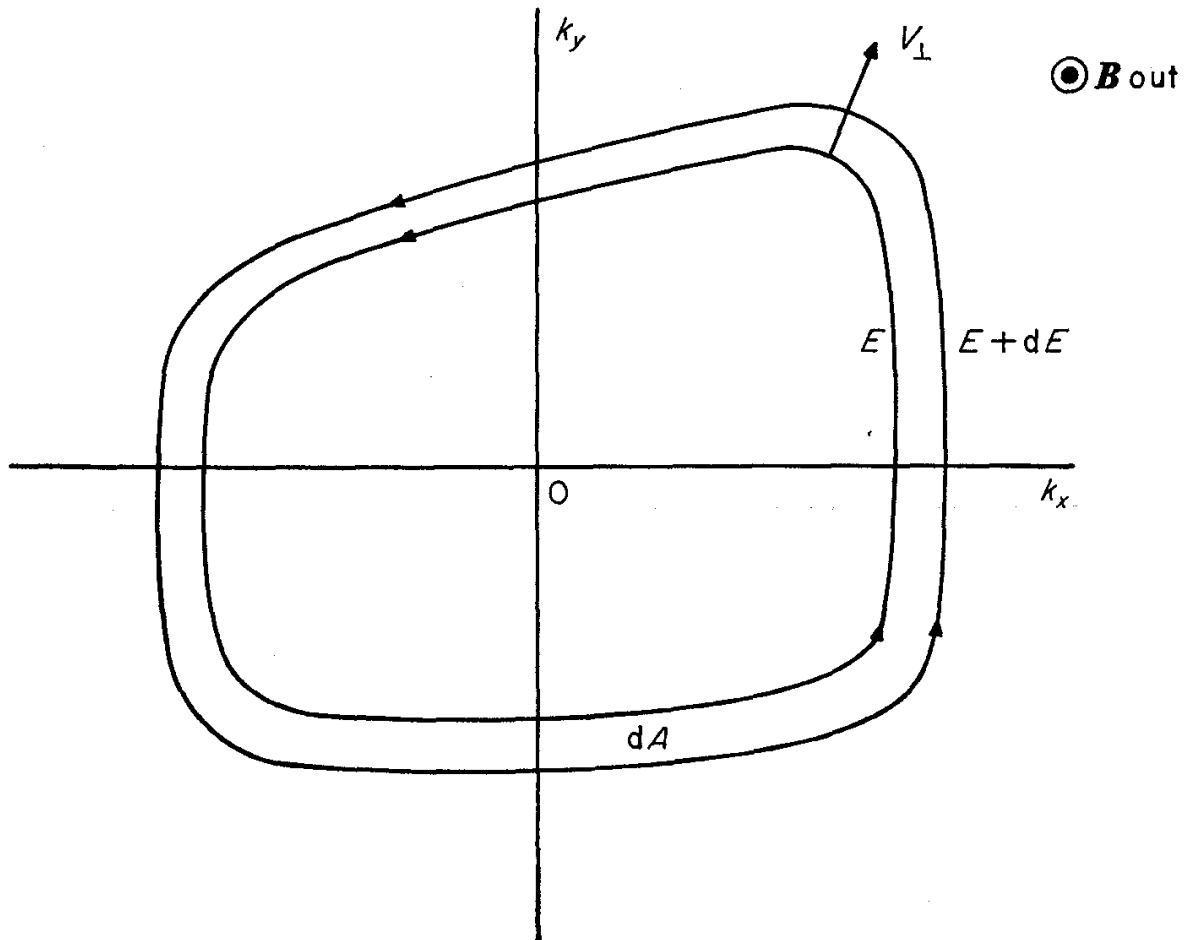
FIG. 5.19   Magnetic orbits

The distance between these two orbits is $dE/|\,(\mathrm{grad}_k E)_\perp\,|$ or $dE/\hbar V_\perp$. $V_\perp$ is the component of the velocity perpendicular to the field. If dk is an increment of length measured along an orbit then the area of the annulus between the orbits is

$$dA = \frac{dE}{\hbar} \oint \frac{dk}{V_\perp} \tag{5.93}$$

$$\therefore \qquad \frac{dA}{dE} = \frac{1}{\hbar} \oint \frac{dk}{V_\perp}$$

The periodic time of the orbit is

$$T = \frac{2\pi}{\omega} = \oint \frac{dk}{|\dot{k}|} = \frac{\hbar}{eB} \oint \frac{dk}{V_\perp} \tag{5.94}$$

From (5.93) and (5.94) the cyclotron frequency is seen to be

$$\omega = \frac{2\pi eB}{\hbar^2} \bigg/ \left(\frac{dA}{dE}\right) \tag{5.95}$$

If the constant energy surfaces are spheres

$$E = \frac{\hbar^2 k^2}{2m^*}$$

(For free electrons substitute m for m^*.) The orbits are now
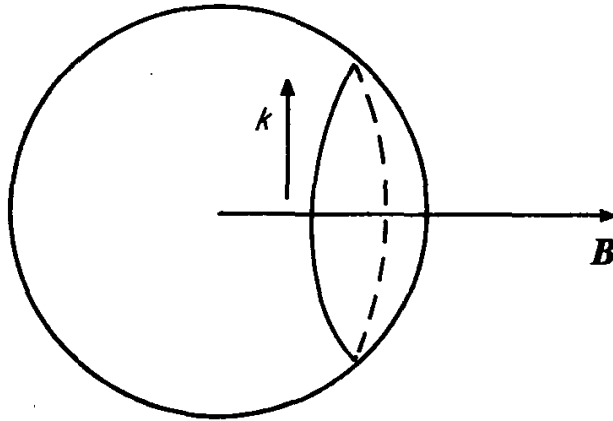
FIG. 5.20   Magnetic orbits for spherical band

circles and if k is the component of the wave number in the plane normal to the field

$$A = \pi k^2 = \pi(2m^*)E/\hbar^2 + \text{constant}$$

$$\frac{dA}{dE} = \pi 2m^*/\hbar^2$$

The cyclotron frequency is the same for all orbits.

$$\omega = eB/m^* \tag{5.96}$$

In general, however, ω is different for each orbit. A 'cyclotron mass' m_c^* for the orbit is defined by the equation

$$m_c^* = \frac{\hbar^2}{2\pi}\left(\frac{dA}{dE}\right) \tag{5.97}$$

so that

$$\omega = \frac{eB}{m_c^*} \tag{5.98}$$

The effects of scattering have been ignored in this discussion. If $B \sim 0.1\, Wbm^{-2}$ a free electron describes a circle in $\sim 10^{-10}$ sec. At room temperature, many collisions per cycle may be expected. However, with pure materials at low temperatures the collision times may be increased so that several circuits may be made with a suitably large field. Experimentally, the frequency is found by microwave absorption. In semiconductors where the charge carriers occupy a small region of a band, the energy surfaces are usually ellipsoidal and it can be shown that all the orbits have the same frequency for a given field direction. The observed resonance line gives information about the energy surface.

The application to metals is more complicated and the reader is referred to the literature for further information (Pippard, 1960).

However, it should be pointed out that the above 'wave-packet' treatment is semi-classical and is not the full story. Elementary quantum ideas suggest that as the motion is periodic perpendicular to B then quantization may be expected to occur. An exact treatment for crystals presents some difficulties but the free-electron case has been examined rigorously and it has been shown that only certain orbits in k-space are allowed and that the energy difference between levels is $\hbar\omega$. These are the 'Landau' levels (Landau, 1930).

§ 5.16 The effective mass approximation

Real crystals contain many imperfections, such as dislocations, vacancies, impurities, etc. Some crystal properties are little effected by these, others are profoundly altered. The cohesive energy and specific heat are among the former, whereas the conductivity of metals at low temperatures and the transport properties of semiconductors are examples of the latter. In general these imperfections may be regarded as localized perturbations of the periodic potential.

In Section 5.14, it was shown how close to an energy maximum or minimum a wave packet moves as a classical particle but with different effective masses along the three principal axes. Intuitively, in the vicinity of an impurity, it would seem to be a reasonable guess to solve the Schrödinger equation:

$$-\frac{\hbar^2}{2}\left[\frac{1}{m_1^*}\frac{\partial^2}{\partial x^2} + \frac{1}{m_2^*}\frac{\partial^2}{\partial y^2} + \frac{1}{m_3^*}\frac{\partial^2}{\partial z^2}\right]\psi + V\psi = E\psi \quad (5.99)$$

If V is the localized potential of an impurity atom, then E may be taken to represent the energy values near the impurity. The crystal periodic potential is 'contained' in the effective mass. This equation is correct when the right interpretation is given, but it certainly requires some justification.

If $\mathscr{H}_0$ is the perfect crystal Hamiltonian the equation to be solved is

$$(\mathscr{H}_0 + V)\psi = E\psi \quad (5.100)$$

The perturbed wave function ψ may be expressed as a sum over all the Bloch functions in all bands. If the perturbation is slowly varying it should be a good approximation to restrict the sum to the Bloch waves from a single band. As V is a localized potential it would seem sensible to express ψ in terms of localized functions. The set of Wannier functions for a band span the same space as the Bloch waves and so in this approximation

$$\psi = \sum_{R_n}\Psi(R_n)a(r - R_n) \quad (5.101)$$

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If equation (5.101) is substituted into (5.100) and the result multiplied on the left by $a^*(r - R_m)$ and integrated, then

$$\sum_{R_n} \Psi(R_n) \int a^*(r - R_m)[\mathscr{H}_0 + V]a(r - R_n) \, d\tau = E\Psi(R_m)$$

$$(5.102)$$

Using (5.66) these equations may be written

$$\sum_{R_n} [\epsilon(R_m - R_n) + V(R_m, R_n)]\Psi(R_n) = E\Psi(R_m) \quad (5.103)$$

$$V(R_m, R_n) = \int a^*(r - R_m)V(a - R_n) \, d\tau$$

The difference equations (5.103) may be simplified by usefully employing the localization of the Wannier functions. When V is slowly varying over several cells the matrix element $V(R_m, R_n)$ is nearly zero when $R_m \neq R_n$. All off-diagonal terms are ignored and the remaining term is, to a good approximation, simply $V(R_m)$.

The set of difference equations (5.103) describes the impurity problem, but is very difficult to solve. Wannier showed how this could often be reduced to a differential equation. The function $\Psi(R_n)$ is defined by (5.101) only at lattice points. Let $\Psi(r)$ be a continuous function which takes the values required by (5.101) at the lattice points. By Taylor's expansion

$$\Psi(r - R_j) = \Psi(r) - R_j \cdot \text{grad } \Psi(r) \ldots \quad (5.104)$$
$$= \exp\left(-R_j \cdot \text{grad}\right)\Psi(r)$$

The first term in (5.103) may be rearranged:

$$\sum_{R_n} \epsilon(R_m - R_n)\Psi(R_n) = \sum_{R_j} \epsilon(R_j)\Psi(R_m - R_j) \quad (5.105)$$

An operator may be defined from $E(k)$ by replacing k by grad/i in (5.65).

$$E\left(\frac{\text{grad}}{i}\right) = \sum_{R_j} \epsilon(R_j) \exp\left[-R_j \cdot \text{grad}\right] \quad (5.106)$$

and so the first term of (5.103) is

$$E\left(\frac{\text{grad}}{i}\right)\Psi(R_m) \quad (5.107)$$

The difference equations may be replaced by the differential equation

$$\left[E\left(\frac{\mathrm{grad}}{i}\right) + V(r)\right]\Psi(r) = E\Psi(r) \qquad (5.108)$$

The wave function Ψ is an 'envelope' of Wannier functions. The differential equation is correct to the same approximation as the difference equation, namely that the potential is slowly-varying and that the wave function can be expressed in terms of a single band.

When the band energy can be expressed as

$$E(k) = E_0 + \frac{\hbar^2}{2}\left[\frac{k_x^2}{m_1^*} + \frac{k_y^2}{m_2^*} + \frac{k_z^2}{m_3^*}\right] + \cdots$$

the equation to be solved is

$$-\frac{\hbar^2}{2}\left[\frac{1}{m_1^*}\frac{\partial^2}{\partial x^2} + \frac{1}{m_2^*}\frac{\partial^2}{\partial y^2} + \frac{1}{m_3^*}\frac{\partial^2}{\partial z^2}\right]\Psi + V\Psi = (E - E_0)\Psi$$
$$(5.109)$$

The equation is identical with (5.99), the energy of the impurity state being measured from E_0.

If an atom, such as arsenic (valence 5), replaces one of the atoms in the semiconductor germanium (valence 4), there will be one valence electron left over. There will be an excess positive charge at the impurity and one 'free' electron to go into the conduction band. This type of impurity is a donor.

The perturbing potential is Coulombic

$$V = -e^2/4\pi\epsilon\epsilon_0 r$$

ϵ is the dielectric constant of the medium. If this potential is considered slowly varying and if a scalar effective mass m^* may be used to describe the bottom of the conduction band, then equation (5.109) is of the hydrogen atom type.

$$-\frac{\hbar^2}{2m^*}\nabla^2\Psi - \frac{e^2}{4\pi\epsilon\epsilon_0 r}\Psi = (E - E_0)\Psi \qquad (5.110)$$

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The energy levels are given by the Rydberg formula.

$$E - E_0 = \frac{-e^4 m^*}{8 h^2 \epsilon^2 \epsilon_0^2 n^2}$$

There are discrete bound states at this depth below the bottom of the conduction band. For germanium a sensible value of m^* is $\sim 0 \cdot 1 m$ and $\epsilon \sim 15$. The corresponding ionization energy of the impurity is $\sim 0 \cdot 005$ eV. (This should be compared with the hydrogen atomic ionization energy of $13 \cdot 6$ eV with $m^* = m$ and $\epsilon = 1$.) These results are in fair agreement with the donor levels in semiconductors.

If there are trivalent impurities such as boron or aluminium in a quadrivalent semiconductor they will act as acceptors as they take up electrons from the valence band leaving holes. The impurity levels lie immediately above the valence band.
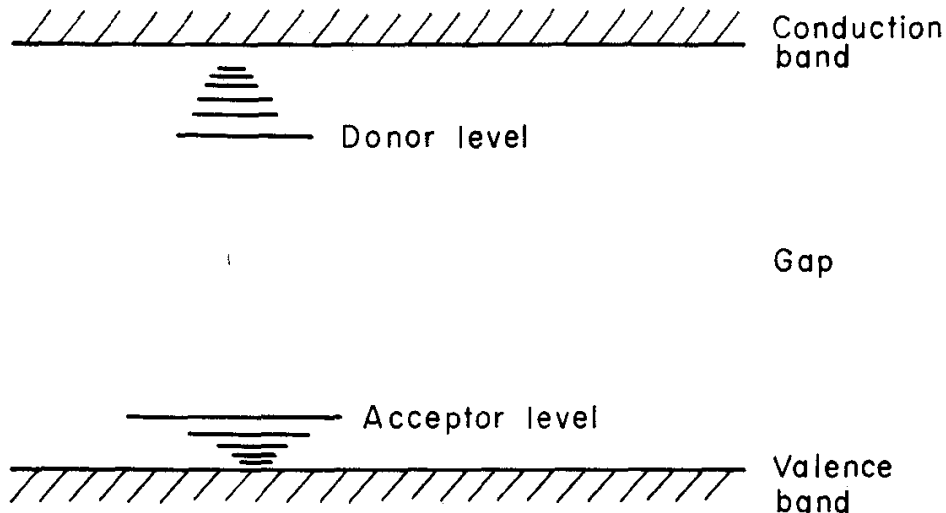
FIG. 5.21

In the absence of impurities the number of electrons in the conduction band is equal to the number of holes in the valence band. If donor atoms are present in any number the electrons will be predominant and the material is said to be n-type. On the other hand, if acceptor atoms are present, then the positive carriers will control the conductivity and the material is p-type. The extrinsic conductivity of an impure specimen is in general

considerably higher than the ideal intrinsic conductivity of the pure material as the acceptor and donor states are ionized much more easily.

The above treatment of donors and acceptors has been greatly simplified to bring out the principles of the problem rather than the complications. Considerably better results are obtained if a non-scalar mass is used (equation (5.109)), but then the Schrödinger equation cannot be solved analytically. (For germanium the absolute minimum of the conduction bands is not at the origin but occurs at the centres of the hexagonal faces of the zone. It is then necessary to define two effective masses.)

An F-centre in an ionic crystal is a similar problem. This may be regarded as an electron bound to a negative ion vacancy.

An electron and a hole may form a bound pair and so generate a set of hydrogen type levels. Frenkel called such a pair an exciton. It can be shown that they would produce a set of levels just below the conduction band in the forbidden gap. These levels have been observed in highly purified germanium.

Problems for Chapter 5

1. The reciprocal lattice primitive cell has a volume $V_b = b_1 . (b_2 \wedge b_3)$. Show that $V_b = (2\pi)^3/V_d$ where V_d is the volume of the direct lattice primitive cell.

2. The reciprocal basis vectors are given by equations (5.2). Invert these relations to give

$$a_1 = \frac{2\pi}{V_b}(b_2 \wedge b_3), \; a_2 = \frac{2\pi}{V_b}(b_3 \wedge b_1), \; a_3 = \frac{2\pi}{V_b}(b_1 \wedge b_2)$$

(This result follows in fact from the symmetry of the definition (5.1).)

3. The two vectors $\left(\frac{1}{h}a_1 - \frac{1}{l}a_3\right)$ and $\left(\frac{1}{h}a_1 - \frac{1}{k}a_2\right)$ may be

used to define the set of planes with Miller indices (hkl). Find the scalar product of the reciprocal lattice vector $K = hb_1 + kb_2 + lb_3$ with each of these vectors. Hence show that K is normal to the (hkl) planes of the real lattice.

4. Given that the function $f(r)$ has the periodicity of the lattice verify that

$$\int f(r)e^{ik\cdot r}\, d\tau = 0$$

unless k is a reciprocal lattice vector. (Note equation (5.7).)

5. The potential $V(r)$ of an electron and the probability density are related by Poisson's equation $\nabla^2 V = e\rho/\epsilon_0$. Both V and ρ are periodic functions and may be expressed as Fourier series.

$$V(r) = \sum_{K_n} V(K_n)e^{-iK_n\cdot r}, \quad \rho(r) = \sum_{K_n}\rho(K_n)e^{-iK_n\cdot r}$$

Show that

$$V(K_n) = -\frac{e}{K_n^2\epsilon_0}\rho(K_n) \qquad K_n \neq 0$$

6. A cubic unit cell containing four lattice points may be chosen for a face-centred cubic lattice. If this cube has a side of length $2a$ a rhombohedral primitive cell may be defined by the basis vectors

$$a_1 = a(0,\ 1,\ 1),\ a_2 = a(1,\ 0,\ 1),\ a_3 = a(1,\ 1,\ 0)$$

$$\text{(Fig. 3.4)}$$

Using equations (5.2) find a set of basis vectors for the reciprocal lattice. Verify that this lattice is body-centred cubic. (The basis vectors for a b.c.c. lattice may be chosen so that $a_1 = a(-1,\ 1,\ 1)$, $a_2 = a(1,\ -1,\ 1)$, $a_3 = a(1,\ 1,\ -1)$. The cube of side $2a$ is twice the size of the primitive cell.)

7. A simple cubic lattice with parameter a has a simple cubic reciprocal lattice with minimum distance $2\pi/a$. The Brillouin zone is a cube. Show that:

 (a) the small group at $k = 0$ is the full cubic group $m3m$;
 (b) the small group at a general point Δ on the k_x-axis is the tetragonal group $4mm$ containing eight elements;

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(c) the small group at a general point Λ on a cube diagonal is the group $3m$ containing six elements.

Find the star of the k-vector for each of these cases. Show that the point X where the k_x-axis meets the zone face and the point R where the diagonal meets the zone corner have the small groups $4/mmm$ (with 16 elements) and $m3m$ (48 elements) respectively.

8. A normalized hydrogen type $(1s)$ wave function may be written

$$(1s) = \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} e^{-\alpha r}$$

The normalized plane wave $e^{ik\cdot r}/(\Omega)^{\frac{1}{2}}$ can be made orthogonal to the $(1s)$ function by the Schmidt process. Ω is the volume of the crystal. Show that the resulting orthogonalized plane wave when $k = 0$ is

$$\psi_{\text{O.P.W.}} = \frac{1}{\sqrt{\Omega}} \left(1 - 8e^{-\alpha r}\right)$$

Note that this new function has a single radical node like a $(2s)$ wave function. Investigate the behaviour of this function when $r \gg 1/\alpha$.

(Herring (1940) introduced the O.P.W. method. In crystals the plane waves are orthogonalized to all the core Bloch waves with the same k-value.)

9. Consider the hypothetical problem of a one-dimensional lattice of like atoms. If there are two electron states close together in the free atom and if these states have s- and p-type symmetry respectively, then on crystal formation each level will form a band. In the tight-binding approximation the wave functions are

$$\Psi_k = A_1 \psi_{1k} + A_2 \psi_{2k}$$

ψ_{1k} and ψ_{2k} are Bloch waves composed of s and p atomic functions respectively. It may be assumed that all the atomic

functions are mutually orthogonal. Show that the two energy bands are given by

$$E(k) = \frac{(H_{11} + H_{22}) \pm [(H_{11} - H_{22})^2 + 4\,|\,H_{12}\,|^2]^{\frac{1}{2}}}{2}$$

where
$$H_{ij} = \int \psi_{ik}{}^* \mathscr{H} \psi_{jk}\,\mathrm{d}\tau$$

By using the substitution $\tan^2 \theta = 4\,|\,H_{12}\,|^2/(H_{11} - H_{22})^2$ show that the lowest band energy function is

$$E_1(k) = \tfrac{1}{2}[H_{11}(1 + \sec \theta) + H_{22}(1 - \sec \theta)]$$

with Bloch waves

$$\Psi_1 = \cos \frac{\theta}{2}\psi_{1k} + i\sin \frac{\theta}{2}\psi_{2k}$$

Find the corresponding solutions for the upper band.

10. In Problem 9, investigate the two cases:

(a) $H_{11} \neq H_{22}$ for all k and

(b) $H_{11} = H_{22}$ for some particular $k = k'$

Show that in case (a) the band edge functions have the same symmetry as $k = 0$ whereas in case (b) the wave function symmetry changes from s-type (or p-type) at $k = 0$ to p-type (s-type) at the band edges. Note that the bands themselves do not cross.

11. Show that the periodic part of a Bloch wave satisfies the equation

$$\left[\mathscr{H} - i\frac{\hbar^2}{m}k \cdot \mathrm{grad}\right]u_{n,k} = \left[E_n(k) - \frac{\hbar^2 k^2}{2m}\right]u_{n,k}$$

n denotes the band. For sufficiently small k the term

$$-i\frac{\hbar^2}{m}k \cdot \mathrm{grad}\ u_{n,k} = \frac{\hbar k}{m} \cdot p u_{n,k}$$

may be treated as a perturbation and the energy found in terms of the solutions at $k = 0$. Obtain the expression for the energy (correct to second-order),

$$E_n(k) - \frac{\hbar^2 k^2}{2m} = E_n(0) + \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|<n|k \cdot p|n'>|^2}{E_n(0) - E_{n'}(0)}$$

$$<n|k \cdot p|n'> = \int u_{n0}{}^*(k \cdot p) u_{n'0} \, d\tau$$

Verify that the effective mass tensor is given by

$$\left(\frac{m}{m^*}\right)_{ij} = \delta_{ij} + \frac{2}{m} \sum_{n'}' \frac{<n|p_i|n'><n'|p_j|n>}{E_n(0) - E_{n'}(0)}$$

(The $k \cdot p$ approximation can be extended to include a general point in the Brillouin zone. When energy bands are degenerate the expression is more complicated.)

12. Show that the momentum eigenfunction (5.78) and the Wannier function are Fourier transforms of one another.

$$W(k') = \frac{\sqrt{N^3}}{\sqrt{\Omega}} \int_{\substack{\text{all} \\ \text{space}}} a(r) e^{-ik' \cdot r} \, d\tau$$

13. Prove that for a symmorphic space group the Wannier function may always be chosen to be a basis for a one-dimensional irreducible representation of the crystal point group if the band is non-degenerate.

(Hint: Equation (5.29) may be assumed.)

14. Consider the linear lattice with spacing a with N cells in the repeating micro-crystal. If the Bloch functions are taken to be normalized plane waves show that the Wannier function at the origin is

$$a(x) = \frac{\sqrt{a}}{\pi} \frac{\sin \pi x/a}{x}$$

(Hint: Convert the sum over the Bloch waves into an integral over the Brillouin zone.)

15. If $\psi(r)$ is an eigenfunction with energy E for an electron in a steady uniform electric field $\mathscr{E}$ show that $\psi(r - R_n)$ is also an eigenfunction with energy $(E + e\mathscr{E} \cdot R_n)$. (This illustrates the 'Stark Ladder system'.)

16. If a magnetic field B is applied along the z-axis the motion

of an electron (charge $-e$) is periodic in the plane $z = $ constant. By the Bohr–Sommerfeld method the phase integral

$$\oint p \, dq = (n + \phi)h$$

n is an interger, ϕ a phase factor. The momentum p conjugate to the position vector r is $\hbar k - eA$. ($B = \text{curl } A$). Show that the permitted orbits have projected areas $(n + \phi)h/eB$ in real space corresponding to

$$(n + \phi)2\pi eB/\hbar \text{ in } k\text{-space}$$

(Hint: integrate equation (5.76) to find k in terms of r. This is a simplified explanation of Landau levels. See also Problem 19.)

17. Show that near the bottom of an s-band in a simple cubic structure the density of states is

$$N(E) = \frac{\Omega}{4\pi^2 a^3 |\beta|^{\frac{3}{2}}} [E - E(0)]^{\frac{1}{2}}$$

where $E(0)$ is the energy at $k = 0$. (Note equation (5.61).)

18. In general the Fermi level E_F in a semiconductor lies in the gap between the valence and conduction bands. At moderate temperatures it may be assumed that $(E - E_F) >> kT$ for energies in the conduction band. Show that the electrons obey the distribution

$$f_e \simeq e^{(E_F - E)/kT}$$

Verify that if $(E_F - E) >> kT$ the holes in the valence band obey

$$f_h = 1 - f_e \simeq e^{(E - E_F)/kT}$$

If scalar effective masses m_e, m_h can be used to describe the conduction and valence bands respectively prove that the product of the concentrations of electrons and holes is a constant at a given temperature independent of the position of the Fermi level. (As long as the stated assumptions are satisfied.)

$$n_e n_h = 4(2\pi kT/h^2)^3 (m_e m_h)^{\frac{3}{2}} e^{-E_g/kT}$$

E_g is the energy gap between bands.

(Hint: Take the zero of energy as the top of the valence band and write

$$n_e = \frac{2}{\Omega} \int_{E_g}^{\infty} N_c(E) f_e \, dE, \quad n_h = \frac{2}{\Omega} \int_{-\infty}^{0} N_v(E) f_h \, dE$$

where $N_c(E)$, $N_v(E)$ are the density of states in the conduction and valence bands respectively. The factor 2 arises by considering spin.)

19. For a spherical energy band, the effective mass equation (5.109) for an electron in a magnetic field may be taken to be

$$\frac{1}{2m^*} \left(\frac{\hbar}{i} \text{grad} + eA \right)^2 \Psi(r) = E\Psi(r)$$

(The energy zero is chosen so that $E_0 = 0$.)

If the magnetic field is in the z-direction it is possible to choose the vector potential $A = (-By, 0, 0)$. Separate the variable y by using the substitution

$$\Psi(r) = e^{i(k_x x + k_z z)} \phi(y)$$

Prove that the resultant equation in y is that of a simple harmonic oscillator of frequency $\omega = eB/m^*$ with equilibrium point at $y_0 = \hbar k_x/eB$. Hence derive the following expression for the energy

$$E = \frac{\hbar^2 k_z^2}{2m^*} + (n + \tfrac{1}{2})\hbar\omega \quad n \text{ positive integer}$$

This result shows that the energy is made up of the kinetic energy parallel to the field and the quantized energy of the motion in the plane perpendicular to the field. These discrete levels are the Landau levels.

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6

Electron Transport Phenomena

§ 6.1 Introduction

This chapter deals with conduction processes in metals. The much smaller conductivities of insulators depends on the ionic motion and is a completely different problem. Semiconductors are not dealt with specifically although it is not difficult to extend the treatment given below to cover most of them. The essential difference is that in metals the electrons are highly degenerate whereas classical statistics frequently apply to the carriers (holes and electrons) in semiconductors. Only the effects of steady fields and of thermal gradients will be discussed and neither photoconductivity nor superconductivity will be mentioned.

In the previous chapter it was shown that in the absence of applied fields an electron in a stationary state in a perfect crystal has an average velocity

$$V(k) = \frac{1}{\hbar} \operatorname{grad}_k E(k) \qquad (5.67)$$

This implies that once an electric current was set up no field would be required to maintain it. The electric resistance would be zero. Clearly this is not correct for real crystals and so the deviations of the lattice from true periodicity must be important in a discussion of transport effects.

When a constant electric field is applied to a perfect crystal

an electron is accelerated so that its wave vector passes periodically through the Brillouin zone in a direction opposed to the field. In Section 5.12 it was stated that in fact this does not happen in a real metal as electron scattering results in a steady state in which the electron distribution is displaced by a fixed amount in k-space. The two main causes of the scattering are:

(i) the thermal lattice vibrations;
(ii) the impurities and lattice imperfections.

(The electron–electron interaction will have some effect, but this is generally small. However, this interaction is important in the theory of superconductivity.)

A detailed study of the mechanics of the electron-lattice interaction is beyond the scope of this book, but a brief discussion will give some insight. (Jones' review article, 1956.) The thermal lattice vibrations give rise to a perturbation which induces electron transitions between different k-states. A vibrational state of the lattice is described by a set of quantum numbers giving the number of phonons in each state with wave vector q (Section 4.5). The scattering of an electron is interpreted as the emission (or absorption) of a phonon by the electron. The electron loses (or gains) the quantum of energy

$$E(k_f) = E(k_i) \mp \hbar\omega \qquad \text{—emission} \quad (6.1)$$
$$+\text{absorption}$$

k_f and k_i are the final and initial electron states respectively. This energy change is very small compared with the electron kinetic energy and may be neglected for most purposes. The electron-lattice collisions are essentially elastic and scattering takes place from one point of an electron constant-energy surface in k-space to another.

Equation 6.1 expresses the conservation of energy. It can also be shown that when a phonon is created (or destroyed) the 'crystal momentum' satisfies the conservation relation,

$$k_f = k_i \mp q + K \qquad (6.2)$$

where K is a reciprocal lattice vector. All the wave vectors are confined to the first Brillouin zone. (Reduced zone scheme. Note (5.82).) A transition for which $K = 0$ is called a normal process (N-process) whereas one with $K \neq 0$ is termed an
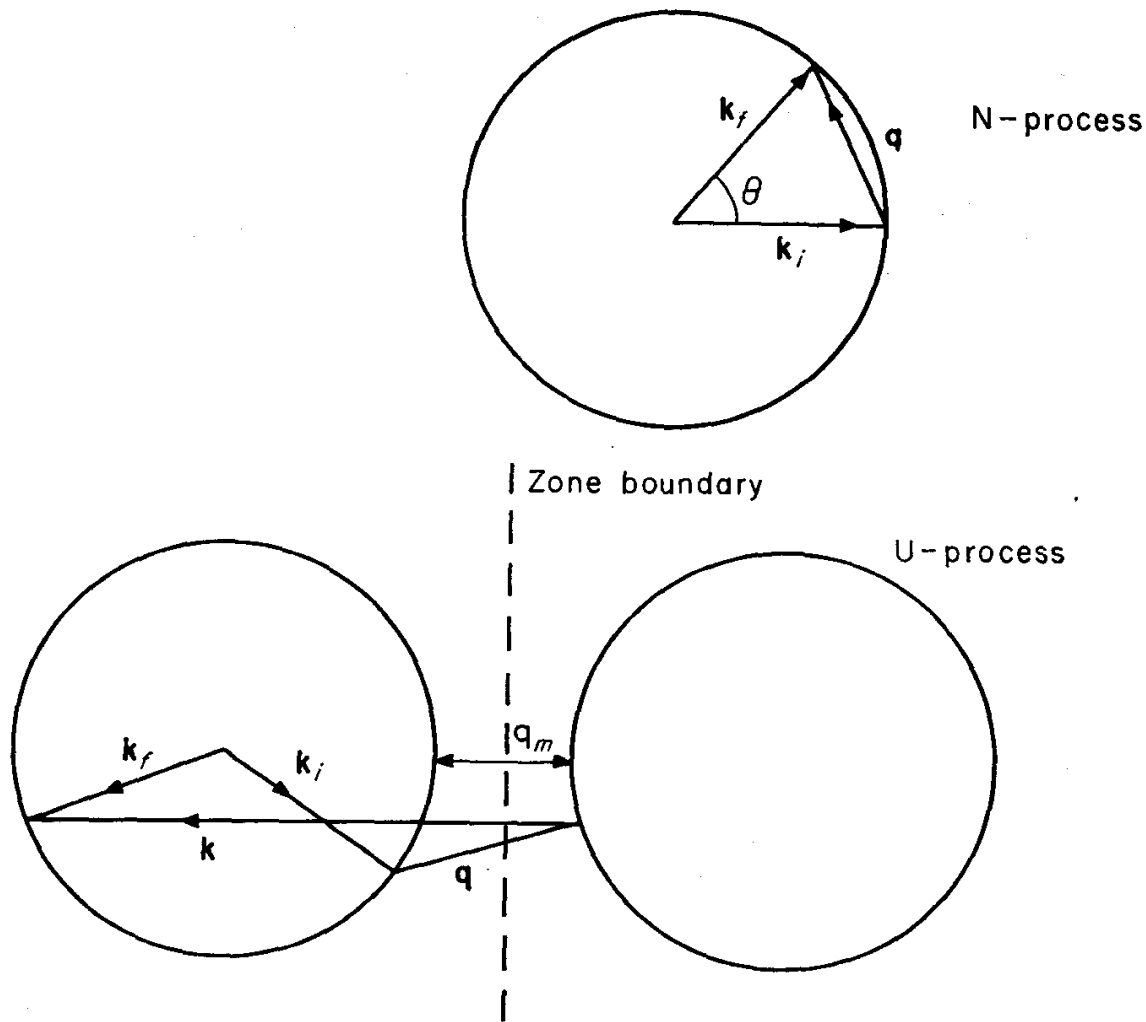
FIG. 6.1   Electron transition on the Fermi surface. Phonon destruction

Umklapp process (U-process). If $k_i \mp q$ lies inside the Brillouin zone the process is normal, but if the vector sum lies outside the zone so that a reciprocal lattice vector K must be added to make k_f lie within then the process is 'Umklapp'. This classification of transitions into normal and Umklapp is somewhat

arbitrary and depends upon the choice of Brillouin zone. In the case of a spherical Fermi-surface (Fig. 6.1) it is convenient to choose a zone with the origin of the sphere coincident with that of the k-axes.

The U-processes produce difficulties in the theory, but if they are neglected many possible transitions are ignored. In the example of the spherical energy band illustrated in Fig. 6.1 if U-processes are ignored then in monovalent metals any scattering through angles greater than $\sim 80°$ is not taken into account. (Problem 2.)

The longitudinal lattice modes are the most important scattering agent, although transverse modes do contribute and may be important in some cases. Intuitively it would be expected that phonons with frequencies so high that they are not thermally excited to any appreciable extent will not contribute to the scattering. This can indeed be verified and the only phonons which need be considered are those for which

$$\hbar\omega \leqslant kT \tag{6.3}$$

Examination of Fig. 6.1 will show that there is a minimum value of the lattice wave vector q_m for a U-process to take place. This value is equal to the minimum distance between the Fermi-surfaces in neighbouring zones. For low temperatures the U-processes may be 'frozen out', but at high temperatures they are dominant. Any further discussion of the electron-phonon interaction would be out of place in an introductory text and the interested reader is referred to Jones' review article (1956).

The scattering in metals at normal temperatures is primarily caused by the thermal vibrations but at very low temperatures the 'residual resistance' due to impurities becomes important. The collisions of conduction electrons with static imperfection is also essentially elastic as the ionic mass is so much greater than that of an electron. Often the resistivity of a metal containing imperfections may be written

$$\rho = \rho_t(T) + \rho_i \tag{6.4}$$

where ρ_t is the resistivity caused by the thermal vibrations and ρ_i is due to imperfections and is temperature independent. Equation (6.4) is an expression of Matthiessen's rule and may be expected to hold if the two sources of scattering are independent of one another. The zero-point thermal vibrations do not contribute to the scattering. This is easily understood when it is remembered that at absolute zero an electron can not absorb phonons as there are no phonons present. Similarly the degenerate electrons can not emit phonons as there are no lower states for the electrons to fall into. In fact the resistance of an ideal metal (pure with no imperfections) would tend to zero as $T \longrightarrow 0$.

§ 6.2 The transport equation

A general theory of electron transport in crystals must not only include the effects of external electric fields but also those of magnetic fields and applied temperature gradients. The problem is analogous to that arising in the theory of transport in the kinetic theory of gases and is solved in a similar manner. The main differences are:

(i) the use of quantum statistics (in metals) instead of classical Boltzmann statistics; and

(ii) that the scattering processes arise from electron-lattice rather than from electron–electron interactions. (In kinetic theory the gas particle collisions produce the scattering.)

At any instant the electron system is described by a single-particle distribution function $f(k, r, t)$ defined so that

$$\frac{1}{4\pi^3} f(k, r, t) \, dk \, d\tau$$

is the average number of electrons in the element dk of reciprocal space and $d\tau$ of real space at the time t. It is assumed that the fields are sufficiently slow varying that $d\tau$ may be chosen

small enough so that the fields and temperature are essentially constant within it and yet large enough that it contains many electrons. In equilibrium in the absence of external fields (or temperature gradients) $f(k, r, t)$ is independent of r and t and is just the Fermi distribution f_0 (2.39). In principle, the transport properties of a conductor are known when the distribution function has been determined under the influence of external fields (or temperature gradient).

Assuming Liouville's theorem is applicable, then in the absence of collisions the distribution function in the neighbourhood of an electron remains constant as the electrons move under the applied fields. That is, the electrons which lie within the six-dimensional volume of phase space $dk\ d\tau$ about k, r at time t will occupy an equal volume about $k + \dot{k}\ dt$, $r + V\ dt$ at time $t + dt$.

i.e. $$\frac{Df}{Dt} = \left(\frac{\partial f}{\partial t}\right)_{r,k} + \dot{r} \cdot \text{grad}_r f + \dot{k} \cdot \text{grad}_k f = 0 \quad (6.5)$$

$\text{grad}_r f$ and $\text{grad}_k f$ denote gradients in real and reciprocal space respectively. In a real crystal the electron-lattice collisions produce a net change in f along an electron trajectory.

$$\left(\frac{\partial f}{\partial t}\right)_c = \left(\frac{\partial f}{\partial t}\right)_{r,k} + \dot{r} \cdot \text{grad}_r f + \dot{k} \cdot \text{grad}_k f \quad (6.6)$$

(Strictly it is only possible to refer to trajectories for classical particles.)

The l.h.s. denotes the rate of change due to scattering. Equation (5.75) may be used to express $\dot{k}$ in terms of the external fields $\mathscr{E}$ and B.

$$\left(\frac{\partial f}{\partial t}\right)_c = \left(\frac{\partial f}{\partial t}\right)_{r,k} + V \cdot \text{grad}_r f - \frac{e}{\hbar}(\mathscr{E} + V \wedge B) \cdot \text{grad}_k f$$
$$(6.7)$$

This is the Boltzmann equation. In the steady state $\left(\frac{\partial f}{\partial t}\right)_{r,k} = 0$.

The collision term is complicated and its evaluation is the major difficulty of the theory although it can simply be ex-

pressed in terms of a transition probability. As the collisions may be assumed to be elastic it is useful to define the probability so that $P(k, k')\, dS'$ is the probability per unit time that an electron in the Bloch state k makes a transition to some empty state k' in the element dS' of the constant energy surface including both k and k'. As defined $P(k, k')$ depends on the density of states on the energy surface. The number of electrons per unit volume leaving the volume element dk for dS' in time dt depends also on the number of electrons in the element dk and the probability that the final state k' is vacant and is given by

$$\frac{1}{4\pi^3} P(k, k') f(k)\, dk\, [1 - f(k')]\, dS'\, dt \qquad (6.8)$$

The total number of electrons leaving dk in unit time for all points on the energy surface is

$$\frac{dk}{4\pi^3} \int_s P(k, k') f(k) [1 - f(k')]\, dS' \qquad (6.9)$$

The integration is over the constant energy surface. Similarly the gain of electrons by dk in unit time is

$$\frac{dk}{4\pi^3} \int_s P(k', k) f(k') [1 - f(k)]\, dS' \qquad (6.10)$$

Clearly the net gain per unit time is

$$\frac{dk}{4\pi^3} \left(\frac{\partial f}{\partial t}\right)_c = \frac{dk}{4\pi^3} \int_s \{P(k', k) f(k') [1 - f(k)]$$
$$- P(k, k') f(k) [1 - f(k')]\}\, dS' \qquad (6.11)$$

The transition probability between two states is the same for either direction.

$$P(k', k) = P(k, k')$$

$$\therefore \qquad \left(\frac{\partial f}{\partial t}\right)_c = \int_s P(k, k') [f(k') - f(k)]\, dS' \qquad (6.12)$$

This is precisely the result that would have been obtained if the exclusion principle had been ignored.

Further progress depends upon the precise form of the probability function $P(k, k')$ and is difficult. The problem is greatly simplified when the collision integral (6.12) can be written in terms of a relaxation time. A function $\tau(k)$ can always be defined by

$$\left(\frac{\partial f}{\partial t}\right)_c = -\frac{f(k, r, t) - f_0(k, r)}{\tau(k)} \qquad (6.13)$$

Here $f_0(k, r)$ corresponds to thermal equilibrium in the absence of applied fields and temperature gradients. As mentioned already, this function is the Fermi function and in the absence of a temperature gradient does not vary with r. In the general case when the temperature varies from point to point then f_0 will depend on r (2.29, 2.41). Of course $\tau(k)$ as defined by (6.13) is not unique but will depend on the applied fields and temperature gradients. However, under certain circumstances $\tau(k)$ to a good approximation is independent of the fields and temperature gradients and it is in these cases that $\tau(k)$ is a true relaxation time. Equation (6.13) states that the 'rate of relaxation' due to collision processes is proportional to the deviation of the function from equilibrium. In the absence of applied fields or temperature gradients Boltzmann's equation is

$$-\frac{f(k, t) - f_0(k)}{\tau(k)} = \left(\frac{\partial f}{\partial t}\right)_{r,k} \qquad (6.14)$$

The solution is

$$f = f_0 + (f_i - f_0)e^{-t/\tau}$$

f_i is the initial value of the distribution function. This result shows that under the collision scattering processes alone, f approaches the equilibrium distribution exponentially with time constant τ.

The introduction of a relaxation time is an approximation but for small deviations of the distribution function from equilibrium (i.e. small fields and temperature gradients) it would appear to be reasonable.

§ 6.3 Electrical conduction and Ohm's law

Suppose a uniform electric field $\mathscr{E}$ is applied in the x-direction and that no magnetic field or temperature gradient is present. All points in the crystal are equivalent and so in the steady state, f is a constant in space and time. Assuming a relaxation time can be defined, Boltzmann's equation becomes

$$-\frac{f(k) - f_0(k)}{\tau(k)} = -\frac{e}{\hbar}\mathscr{E} \cdot \text{grad}_k f(k) \qquad (6.15)$$

i.e. $$f(k) = f_0(k) + \frac{e}{\hbar}\mathscr{E}\tau(k)\frac{\partial f}{\partial k_x}(k) \qquad (6.16)$$

The fields that can be maintained in metals are weak and to first order in the field, f on the r.h.s. may be replaced by f_0.

$$f(k) = f_0(k) + \frac{e}{\hbar}\mathscr{E}\tau(k)\frac{\partial f_0}{\partial k_x}(k) + \dots \qquad (6.17)$$

The linear term is responsible for Ohm's law and the higher terms produce deviations from it. The internal high fields at p–n junctions have enabled the effects of the higher terms to be observed. Using Taylor's theorem (6.17) may be expressed as

$$f(k) = f_0\left(k_x + \frac{e\mathscr{E}\tau}{\hbar}, k_y, k_z\right) \qquad (6.18)$$

If τ is independent of k the distribution moves bodily a distance $e\mathscr{E}\tau/\hbar$ in k-space opposed to the field (Fig. 5.12). In fact it is only really necessary to assume that τ is a constant in the neighbourhood of the Fermi surface as the second term in the expansion (6.17) may be written

$$\frac{e\mathscr{E}\tau}{\hbar}\frac{\partial E}{\partial k_x}\frac{\partial f_0}{\partial E}$$

and is zero except near the Fermi surface.

The current density j is

$$j = -\frac{e}{4\pi^3}\int V(k)f(k)\,dk \qquad (6.19)$$

The integral is over all partially filled bands. The first term in (6.17) represents equilibrium and does not contribute to the current.

$$j_x = -\frac{e^2}{4\pi^3}\frac{\mathscr{E}}{\hbar}\int V_x\tau\frac{\partial E}{\partial k_x}\frac{\partial f_0}{\partial E}\,\mathrm{d}k \qquad (6.20)$$

The integration over k-space may be expressed as a combination of an integration over the energy combined with an integration over surfaces of constant energy. This enables the delta-function characteristics of $\left(-\dfrac{\partial f_0}{\partial E}\right)$ to be utilized (2.40–2.47). With $\mathrm{d}k = \mathrm{d}S\,\mathrm{d}E/|\,\mathrm{grad}_k E\,|$

$$j_x = \frac{e^2\mathscr{E}}{4\pi^3\hbar^2}\int_F \tau\left(\frac{\partial E}{\partial k_x}\right)^2\frac{1}{|\,\mathrm{grad}_k E\,|}\,\mathrm{d}S \qquad (6.21)$$

The integral is over the Fermi surface and is correct to first order for degenerate electrons in metals although it will not apply to all semiconductors. The conductivity tensor $\boldsymbol{\sigma}$ is defined by

$$\boldsymbol{j} = \boldsymbol{\sigma}\mathscr{E} \qquad (6.22)$$

For a material with no symmetry properties $\boldsymbol{\sigma}$ is symmetric with six distinct components. Many metals have cubic symmetry and for these $\boldsymbol{\sigma}$ is a diagonal tensor with one component.

$$\sigma = \frac{e^2}{12\pi^3\hbar^2}\int_F \tau\,|\,\mathrm{grad}_k E\,|\,\mathrm{d}S \qquad \begin{matrix}\text{Cubic}\\\text{metals}\end{matrix} \qquad (6.23)$$

If τ is a true relaxation time then σ is independent of the applied field and Ohm's law is verified for weak fields ($<10^8 Vm^{-1}$). Equation (6.23) shows that the conductivity depends only upon the properties of the electrons at the Fermi surface. The electrons deep within the Fermi surface are prevented by the exclusion principle from being scattered. If τ is taken as constant over the Fermi surface and the band assumed to be of standard form so that

$$E(k) = \hbar^2 k^2/2m^*$$

then it is easily shown that

$$\sigma = e^2 n \tau(k_F)/m^*$$
(6.24)

where the electron concentration per unit volume is, for highly degenerate electrons

$$n = \frac{1}{4\pi^3}\int_0^{k_F} f_0(k) \; \mathrm{d}k \simeq \frac{k_F^3}{3\pi^2}$$
(6.25)

It is worthwhile observing that n is the total number of conduction electrons per unit volume as all electrons are accelerated by the field, but as only those electrons at the Fermi surface are scattered then it is this particular relaxation time which is important. Also, it is interesting to note that the Fermi statistics have a decisive effect upon the electron specific heat (2.5) but not upon the electrical conductivity. In the case considered, where the band may be approximated by one of standard form with a k-independent relaxation time, the expression for the conductivity has the same form as that obtained by a classical treatment.

A mean free path l is defined by

$$l = V(k_F)\tau(k_F)$$
(6.26)

This simple one-band model may be expected to be satisfactory for the monovalent metals (alkalis and noble metals) and then l may be calculated from the observed value of the conductivity. For lithium $l \sim 10^{-8}m$. A 'two-band' model has been used to explain transport phenomena in the transition metals while a multi-band model is probably more appropriate for semi-conductors.

When a current flow is set up the electrons gain kinetic energy from the field and in the steady state this energy is irreversibly transferred to the lattice in the form of Joule heat. The electron-lattice collisions are not really elastic (6.1). If the theory above was extended to include second order terms in the field then Joule heating would be included, but the energy dissipation by the lattice must be considered if a steady state is to be obtained.

The conductivity is not a constant but decreases with rising temperature owing to the variation of the relaxation time. $1/\tau$ is proportional to the number of phonons present and at high temperatures $(T > \theta_D)$ this is proportional to T. So in this case the resistivity $1/\sigma$ is directly proportional to the absolute temperature. At low temperatures $(T << \theta_D)$ a detailed argument shows that the resistivity is proportional to T^5.

§ 6.4 Thermal effects

A temperature gradient gives rise to energy transport (or heat flow) as well as to a thermoelectric current. Suppose that a uniform electric field is applied along the x-axis together with a constant temperature gradient $\dfrac{\mathrm{d}T}{\mathrm{d}x}$. The distribution function is no longer a constant in space and in the steady state Boltzmann's equation is

$$V_x \frac{\partial f}{\partial x} - \frac{e}{\hbar} \mathscr{E} \frac{\partial f}{\partial k_x} = -\frac{f - f_0}{\tau} \qquad (6.27)$$

If terms above first order in the field and temperature gradient are ignored

$$f = f_0 + \frac{e}{\hbar} \mathscr{E} \tau \frac{\partial f_0}{\partial k_x} - \tau V_x \frac{\partial f_0}{\partial x} \qquad (6.28)$$

The variation with x arises from the dependence of the temperature on position (2.39, 2.51).

$$\frac{\partial f_0}{\partial x} = \frac{\mathrm{d}T}{\mathrm{d}x} \frac{\partial f_0}{\partial T}$$

$$= -\frac{\mathrm{d}T}{\mathrm{d}x} \frac{\partial f_0}{\partial E} \left[\frac{\mathrm{d}E_F}{\mathrm{d}T} + \frac{E - E_F}{T} \right] \qquad (6.29)$$

$$\therefore \qquad f = f_0 + \frac{\tau}{\hbar} \frac{\partial E}{\partial k_x} \frac{\partial f_0}{\partial E} \left[e\mathscr{E} + \frac{\mathrm{d}T}{\mathrm{d}x} \left\{ \frac{\mathrm{d}E_F}{\mathrm{d}T} + \frac{E - E_F}{T} \right\} \right]$$

The current density is then (6.19) (see Jones' review)

$$j_x = e\left\{\left[e\mathscr{E} - \left(\frac{E_F}{T} - \frac{dE_F}{dT}\right)\frac{dT}{dx}\right]K_0 + \frac{1}{T}\frac{dT}{dx}K_1\right\} \quad (6.30)$$

with

$$K_n = \frac{-1}{4\pi^3\hbar^2}\int E^n\left(\frac{\partial E}{\partial k_x}\right)^2\tau(k)\frac{\partial f_0}{\partial E}\,dk \quad (6.31)$$

This result shows that a temperature gradient acting alone will give rise to an electric current. That is, a thermoelectric effect is predicted. The electronic contribution to the energy transport per unit area is

$$u = \frac{1}{4\pi^3}\int E(k)V(k)f(k)\,dk \quad (6.32)$$

(In the presence of an electric field the value of $E(k)$ depends upon position. See Fig. 5.17.)

In the case discussed here

$$U_x = -\left[e\mathscr{E} - \left(\frac{E_F}{T} - \frac{dE_F}{dT}\right)\frac{dT}{dx}\right]K_1 - \frac{1}{T}\frac{dT}{dx}K_2 \quad (6.33)$$

At first glance this may appear to be the heat flow but this is not strictly correct. In the absence of external work the heat δQ added to a system is equal to the increase in internal energy δU minus the increase in the free energy. If the number of electrons increases by δN in a region of the metal where the chemical potential (partial potential) is ζ then

$$\delta Q = \delta U - \zeta\delta N \quad (6.34)$$

A free energy current may be defined by

$$\zeta\frac{1}{4\pi^3}\int V(k)f(k)\,dk \quad (6.35)$$

For electrons, the chemical potential is simply the Fermi energy E_F. This free energy current is clearly dependent on there being a particle current, but the heat flow is not.

The true heat flow per unit area is

$$Q = \frac{1}{4\pi^3}\int\{E(k) - E_F\}V(k)f(k)\,dk \quad (6.36)$$

The electronic thermal conductivity is defined when the crystal is in an open electrical circuit so that no current flows. The electrons flowing down the temperature gradient are balanced by an equal number with slightly lower energies flowing the other way.

$$\kappa = \left[-Q_x \Big/ \frac{\mathrm{d}T}{\mathrm{d}x} \right]_{j=0} \qquad (6.37)$$

Clearly in this case there is no distinction between energy transport and heat transport. Equations (6.30) and (6.33) may be combined to eliminate the field $\mathscr{E}$.

$$U_x = Q_x = \left(\frac{K_1{}^2}{K_0} - K_2 \right) \frac{1}{T} \frac{\mathrm{d}T}{\mathrm{d}x} \qquad (6.38)$$

and

$$\kappa = \left(K_2 - \frac{K_1{}^2}{K_0} \right) \frac{1}{T}$$

In metals, the delta-function property of $\left(-\dfrac{\partial f_0}{\partial E} \right)$ may be employed to write K_n as an expansion in T (2.47).

$$K_n = E_F^n \alpha(E_F) + \frac{\pi^2}{6}(kT)^2 \frac{\mathrm{d}^2}{\mathrm{d}E_F^2} (E_F^n \alpha(E_F)) + \ldots$$

$$(6.39)$$

with

$$\alpha(E_F) = \frac{1}{4\pi^3\hbar^2} \int_F \left(\frac{\partial E}{\partial k_x} \right)^2 \frac{\tau(k)}{\mid \mathrm{grad}_k E \mid} \, \mathrm{d}S \qquad (6.40)$$

The integral is over the Fermi surface. If only the first term in (6.39) is used the thermal conductivity vanishes. To obtain a non-zero thermal conductivity it is necessary to include the second order terms and to first order in T

$$\kappa = \frac{\pi^2}{3} k^2 T \alpha(E_F) \qquad (6.41)$$

Once again it is demonstrated that the electron transport phenomena depend upon the electron properties at the Fermi surface.

The electric conductivity is defined under isothermal conditions. From (6.22) and (6.30)

$$\sigma = e^2 K_0 \qquad (6.42)$$

A non-vanishing electrical conductivity is obtained from the first term in the expansion of K_0 and to first order in T

$$\sigma = e^2 \alpha(E_F) \qquad (6.43)$$

When $\alpha(E_F)$ is eliminated from (6.41) and (6.43)

$$\kappa = \sigma L T \qquad (6.44)$$

where L is the Lorenz number $(\pi^2 k^2 / 3e^2) = 2 \cdot 45 \cdot 10^{-8}$ watt. ohm.deg^{-2}. This is the well-known Wiedemann–Franz law. ($\kappa/\sigma T$ is the Wiedemann–Franz ratio.) This law showing that $\kappa \propto \sigma T$ can also be derived using Boltzmann statistics although the Wiedemann–Franz ratio has a different value in this case. It is important to realize that equation (6.44) has been derived without reference to a specific band model and applies to all metals. For most metals the thermal conductivity is almost entirely due to the electrons and the observed values are in quite good agreement with the Lorenz number for a wide range of metals at room temperature. The relation (6.44) between the electrical and thermal conductivities is a consequence of the 'unique relaxation time' assumption. Whenever a single relaxation time can not be defined then deviations may be expected. This does frequently happen.

If a temperature gradient exists in a conductor in open circuit an electric field is produced. The relation between the field and a temperature gradient along the x-axis is

$$\mathscr{E}_x = -\mu \frac{dT}{dx} \qquad (6.45)$$

μ is the Thomson coefficient.

Equation (6.30) clearly illustrates this effect and may be used to evaluate the Thomson coefficient. In the absence of an electric current

$$\mathscr{E}_x = -\frac{1}{e}\left[-\left(\frac{E_F}{T} - \frac{dE_F}{dT}\right) + \frac{1}{T}\frac{K_1}{K_0}\right]\frac{dT}{dx} \qquad (6.46)$$

The Thomson coefficient is

$$\mu = \frac{T}{e}\left[\frac{d}{dT}\left(\frac{E_F}{T}\right) + \frac{1}{T^2}\frac{K_1}{K_0}\right] \qquad (6.47)$$

A more significant parameter is the absolute thermoelectric power S which may be defined by

$$S = \int_0^T \frac{\mu}{T}dT \qquad (6.48)$$

All the thermoelectric effects may be derived from S.

$$S = \frac{1}{eT}\left(E_F - \frac{K_1}{K_0}\right) \qquad (6.49)$$

Equation (6.39) may be used to express K_n and as in the case of thermal conductivity second order terms must be included if a non-vanishing result is to be obtained

$$S = -\frac{\pi^2 k^2 T}{3e}\left[\frac{1}{\sigma(E)}\frac{d\sigma(E)}{dE}\right]_{E_F} \qquad (6.50)$$

where

$$\sigma(E) = \frac{e^2}{4\pi^3\hbar^2}\int_E \left(\frac{\partial E}{\partial k_x}\right)^2 \frac{\tau(k)}{|\operatorname{grad}_k E|}\,dS \qquad (6.51)$$

$\sigma(E)$ represents the 'conductivity' of a metal with Fermi level at E (see (6.21)). Equation (6.50) does not apply to semi-conductors although it does apply to metals over a wide temperature range. Unfortunately it is difficult to use in practice as it is not only necessary to know the value of $\sigma(E_F)$ but also the detailed variation of σ with the energy. This implies a knowledge of the energy dependence of the relaxation time in the neighbourhood of the Fermi surface. It can be shown that when the scattering is produced by lattice vibrations a reasonable choice is $\tau \propto E^{3/2}$ if the band is taken to be of standard form. Then

$$S = -\frac{\pi^2 k^2 T}{eE_F} \qquad (6.52)$$

If $E_F \sim 5eV$ and $T \sim 300°K$ (room temperature) then $S \sim -5 \cdot 10^{-6}V \cdot \deg^{-1}$. Thermoelectric powers of this order are found for metals at room temperature. It should be noted that in contrast to the electric and thermal conductivities, the thermoelectric power is linear in the charge (This holds true for semiconductors.) and so the sign depends partly upon whether the dominant carriers are electrons or holes. The alkali metals (except lithium) all have negative thermoelectric powers showing that the carriers are electrons as expected. It is not necessary to have hole-conduction to produce a positive thermoelectric power. If $\left(\dfrac{1}{\sigma}\dfrac{d\sigma}{dE}\right)_{E_F}$ is itself negative then electron carriers will produce a positive value for S. This is probably the explanation of the positive values observed for lithium and the noble metals. Antimony has a positive thermoelectric power and this is due to hole conduction. For further details the reader is referred to Jones' review (1956).

§ 6.5 Magnetic effects

The two most important phenomena associated with a magnetic field are the Hall effect and the magnetoresistance effect. When a magnetic field is applied to a current carrying conductor perpendicular to the charge flow a voltage is produced perpendicular to both the field and the current. This is the Hall effect and the voltage is the Hall voltage. Under the same conditions the electrical resistance is increased. This is the transverse magnetoresistance effect. (There is also a longitudinal magneto-resistance effect when the magnetic field is parallel to the current.)

When an electric field $\mathscr{E}$ and a magnetic field with induction $\boldsymbol{B}$ are applied under isothermal conditions, the steady-state Boltzmann equation is

$$f = f_0 + \frac{e\tau}{\hbar}(\mathscr{E} + \boldsymbol{V} \wedge \boldsymbol{B}) \cdot \operatorname{grad}_k f \qquad (6.53)$$

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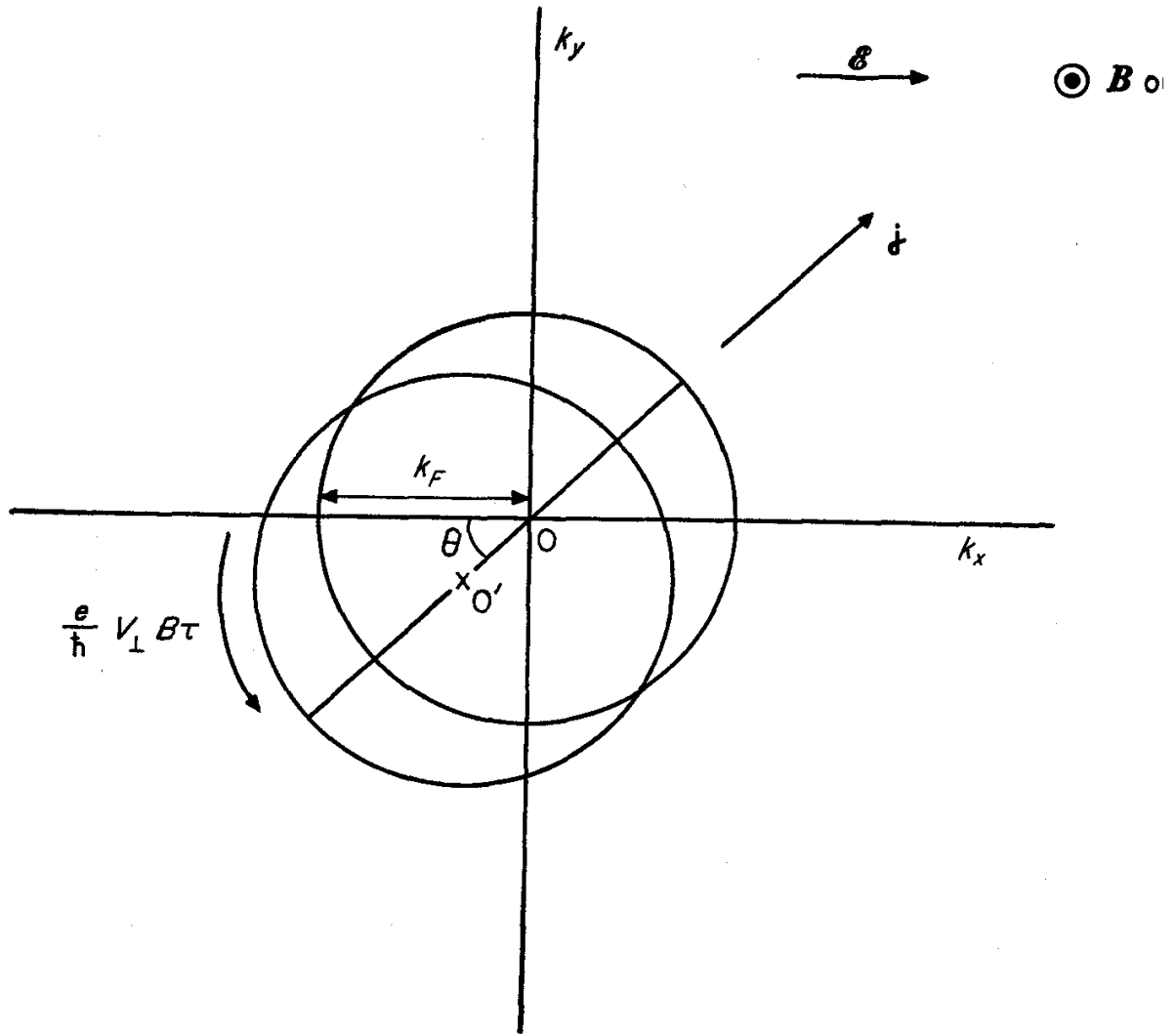
FIG. 6.2 Steady-state distribution in the presence of both
electric and magnetic fields

This equation can be solved, but the algebra is slightly more involved than the previous cases and instead a more intuitive argument will be given. The simplest case of a band of standard form is considered. An electric field alone shifts the whole distribution a distance $e\mathscr{E}\tau/\hbar$ in k-space against the field. τ is the relaxation time at the Fermi surface. This disturbed distribution represents a current parallel to $\mathscr{E}$. A magnetic field rotates the distribution about an axis parallel to B. With high fields

at very low temperatures several revolutions may be made (Cyclotron resonance. Section 5.15) but at higher temperatures lattice scattering results in a steady state and the displacement at the Fermi surface is

$$\delta k = \frac{e}{\hbar} V_\perp B \tau \qquad (6.54)$$

$V_\perp$ is the velocity component at the Fermi surface perpendicular to the field. The combined effect of the electric and magnetic fields is to produce a simultaneous translation and rotation of the spherical distribution so that the average position of the centre of the sphere is off the axis at o' (Fig. 6.2). (Ziman 1963).

The new steady state corresponds to a current at an angle θ to the electric field. This is the Hall angle and $\theta \sim eV_\perp \tau B / \hbar k_F$. For a band of standard form $\theta \sim \omega \tau$ where $\omega = eB/m^*$ is the cyclotron frequency. In practice the Hall effect is observed for

$\odot$ **B** out
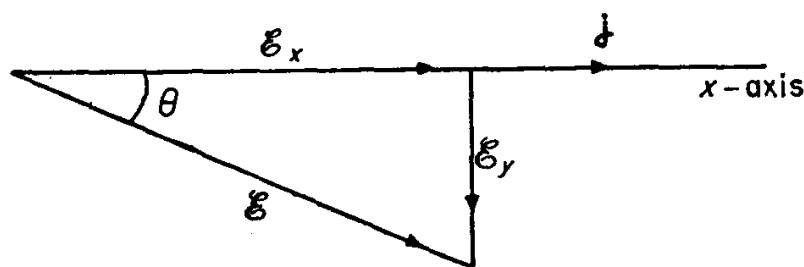
FIG. 6.3

a wire filament (along the x-axis say) so that the current direction can not change. The electrons deflected by the magnetic field build up on the sides of the filament so that a transverse electric field is produced. This Hall field balances **B** and the magnitude is such that the angle between the total electric field and the current remains θ without disturbing the distribution.

The Hall field is

$$\mathscr{E}_y = -\mathscr{E}_x \theta \qquad \theta \text{ small}$$
$$= -\mathscr{E}_x \frac{eB}{m^*}\tau$$

The Hall constant R is defined by

$$R = \frac{\mathscr{E}_y}{jB} = -\frac{\mathscr{E}_x}{j}\frac{e}{m^*}\tau$$

For a band of standard form

$$\sigma = \frac{j}{\mathscr{E}_x} \quad \text{with} \quad \sigma = e^2 n\tau/m^* \qquad (6.55)$$

$$\therefore \qquad R = -\frac{1}{ne}$$

The sign of the Hall coefficient is the same as that of the carriers. In materials where a single standard band is a good approximation a measurement of the Hall effect gives the number of carriers. The monovalent metals have $R \sim -10^{-4} \text{cm}^3/\text{coulomb}$ in fairly good agreement with (6.55).

The transverse magnetoresistance is measured by the relative change in the resistivity. As $\mathscr{E}_x$ and j are unchanged in this approximation (zero-order in kT/E_F) the magnetoresistance is zero for a band of standard form.

A more complete treatment including terms second order in kT/E_F shows that there is a very small magnetoresistance proportional to B^2 for a simple band. Many metals show a magnetoresistance proportional to B^2 but larger by a factor of $\sim 10^5$. This may be explained by assuming either two overlapping bands of standard form or a single anisotropic band, and in these cases there is a magnetoresistance effect to zero order in kT/E_F. It is interesting to note that sodium has a very small magnetoresistance whereas the effect in lithium is quite large. This implies that the Fermi surface in lithium is not spherical, a point already suggested by its positive thermoelectric power.

Problems for Chapter 6

1. Consider a model in which a crystal is regarded as a lattice surrounded by a classical electron gas with n electrons per unit volume. In equilibrium in the absence of external fields the average electron velocity $V = 0$ but when an electric field $\mathscr{E}$ is applied in the positive x-direction the electrons will be accelerated. If a relaxation time τ may be used to characterize the electron-lattice collisions then it may be assumed that

$$m\frac{dV}{dt} + \frac{m}{\tau}V = -e\mathscr{E}$$

Show that the solution of this equation with the given initial condition is

$$V_x = -\frac{e\mathscr{E}\tau}{m}, \quad V_y = V_z = 0 \qquad t >> \tau$$

Derive an expression for the current density in terms of n, e, τ, m and $\mathscr{E}$ and verify that the conductivity is

$$\sigma = ne^2\tau/m$$

(Compare this result with (6.24).)

2. Show that for a band of standard form the angle of scattering in an N-process is given by

$$|\boldsymbol{q}| = 2k_F \sin\frac{\theta}{2}$$

where $\boldsymbol{q}$ is the phonon wave vector and k_F is the magnitude of the electron wave vector on the Fermi sphere. If the phonon Brillouin zone is approximated by a sphere of equal volume show that the maximum angle of scattering by an N-process in monovalent metals is

$$\theta_m = 2\sin^{-1}(2^{-2/3}) \sim 80°$$

3. In anisotropic crystals Ohm's law takes the form

$$j_l = \sigma_{lm}\mathscr{E}_m \qquad l = 1, 2, 3$$

The conductivity is a second order tensor. Show how the symmetry of a cubic crystal demands that the conductivity takes the diagonal form

$$\begin{pmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{pmatrix}$$

(Hint — Consider an electric field first along the y-axis and then along the negative y-axis and show that $\sigma_{xy} = -\sigma_{xy}$, etc.)

4. Starting from equation (6.19) show that in a crystal with no special symmetry properties the elements of the conductivity tensor are given by

$$\sigma_{ij} = \frac{e^2}{4\pi^3\hbar^2}\int_F \tau \frac{\left(\frac{\partial E}{\partial k_i}\right)\left(\frac{\partial E}{\partial k_j}\right)}{|\,\mathrm{grad}_k E\,|} \, \mathrm{d}S$$

Note that the tensor is symmetric about the leading diagonal.

5. In a non-degenerate semiconductor f_0 is the classical distribution function $Ae^{-E/kT}$ where A is some constant. If the conduction band is of standard form with effective mass $m_e{}^*$ show that the electron contribution to the conductivity is

$$\sigma_e = e^2 n_e \bar{\tau}_e / m_e{}^*$$

where n_e is the total number of conduction band electrons and the mean relaxation time is defined by

$$\bar{\tau}_e = \int_{E_g}^{\infty} \tau(E)(E - E_g)^{3/2} e^{-E/kT} \, \mathrm{d}E \bigg/ \int_{E_g}^{\infty} (E - E_g)^{3/2} e^{-E/kT} \, \mathrm{d}E \quad (a)$$

The top of the valence band is taken as the zero of energy and E_g is the energy gap. $\tau(E)$ is assumed not to vary over a surface of constant energy.

The holes also contribute to the current and the total conductivity is

$$\sigma = e^2 \left(\frac{n_e \bar{\tau}_e}{m_e{}^*} + \frac{n_h \bar{\tau}_h}{m_h{}^*} \right)$$

n_h is the total number of holes and $m_h{}^*$ the hole effective mass. Find the expression for $\bar{\tau}_h$ corresponding to (a).

$\Bigg($ Hint — It may be assumed that the conduction and valence bands extend to plus and minus infinity respectively. Also

$$\int_0^\infty E^{3/2} f_0 \, \mathrm{d}E = \frac{3kT}{2} \int_0^\infty E^{1/2} f_0 \, \mathrm{d}E \Bigg)$$

6. The motion of an electron state in k-space under the action of both electric and magnetic fields is given by

$$\mathbf{k} = -\frac{e}{\hbar}(\mathscr{E} + \mathbf{V} \wedge \mathbf{B})$$

Suppose $\mathscr{E} = (\mathscr{E}, 0, 0)$ and $\mathbf{B} = (0, 0, B)$. If the band is taken to be of standard form show that after time t the centre of the spherical distribution is given by

$$k_x = -\frac{\mathscr{E}m^*}{\hbar B} \sin \omega t$$

$$k_y = -\frac{\mathscr{E}m^*}{\hbar B}(1 - \cos \omega t)$$

$$k_z = 0$$

where $\omega = eB/m^*$. Verify that the separation of any two states remains constant throughout the motion. This shows that the distribution behaves as a 'hard sphere'. By considering the motion of two states initially at equal distances from the origin lying on the positive and negative x-axis respectively show that the angle through which the distribution is rotated is $\theta = \omega t$.

7. Suppose in the previous question the electric and magnetic fields are parallel. Find the position of the centre of the spherical distribution at time t. Explain why in this model the longitudinal magnetoresistance is zero.

References and further reading

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7

Cohesion

§ 7.1 Solid types

The problem of solid cohesion has proved itself to be one of the most difficult to answer satisfactorily. Qualitatively it is certainly possible to understand why solids occur. There are short-range attractive forces between atoms and if the temperature is sufficiently low so that these forces are more important than the effects of thermal agitation the atoms will condense to form a solid. One of the fundamental questions a complete solid state theory must answer is, 'Why does an assembly of atoms generally form a periodic structure in the lowest energy state?' To date no complete answer has been given and it is necessary to accept the periodicity as a fact and then attempt to calculate the energy of the lattice as a function of the lattice parameter.

The cohesive energy of a solid is defined as the energy of the crystal in the lowest energy state at absolute zero minus the sum of the ground state energies of the isolated atoms and is a negative quantity. The magnitude of the cohesive energy is called the binding energy (or heat of sublimation) and is equal to the work required to separate the crystal into its constituent atoms. For a macroscopic crystal for which the surface effects may be ignored, the cohesive energy is proportional to the crystal volume and may sensibly be expressed in electron volts per atom or per molecule. (Sometimes expressed in kcal per mole and 23·052 kcal per mole is equivalent to 1 eV per molecule.)

In principle the crystal energy may be obtained by finding the expectation value of the many-particle Hamiltonian 1.10 (including both electrons and ions) regarding the ions as fixed. In this way the crystal energy is found as a function of the ionic separation. Of course, to do this accurately it is necessary to express the many particle wave function as a sum of determinantal wave functions. This procedure has proved most difficult in practice and resort has to be made to more approximate methods.

Solids may be roughly classified by the strength and nature of their cohesive forces into five major types. They are:

(*a*) molecular crystals such as solid nitrogen with binding energies of up to 0·1 eV per molecule;

(*b*) hydrogen-bonded crystals such as ice with binding energies of about 0·5 eV per molecule;

(*c*) ionic crystals such as sodium chloride with binding energies of about 5–10 eV per molecule;

(*d*) valence crystals of which diamond is a good example with binding energies of the order of 10 eV per molecule, and

(*e*) metals with binding energies of 1–5 eV per molecule.

This classification is somewhat artificial and many solids fall into intermediate categories. An example is zinc sulphide which is both ionic and valence-like in character. The rest of this chapter is devoted to a semi-quantitative description of these five main types of solid.

§ 7.2 Molecular crystals

Molecular crystals are very weakly bound and both the melting and boiling points are low. This type of binding is one of the easiest to understand and is the source of the cohesion in crystals composed of inert molecules or atoms. Interesting examples are the rare gases which crystallize in a face-centred cubic structure.

When two neutral atoms or molecules are a few Ångströms apart so that their wave functions essentially do not overlap there is a weak attraction between them. This van der Waal attraction is caused by a mutual polarization of the atoms and is the main cause of binding in molecular crystals.

If a neutral atom is placed in an electric field $\mathscr{E}$ the centre of the distribution shifts from the nucleus so producing a dipole. This effect is normally quite small as the applied field is small compared with the forces inside the atom. A detailed study shows that the average induced dipole moment is then proportional to $\mathscr{E}$. When the field is due to a mutually induced dipole moment on another atom distance r from the first then $\mathscr{E} \propto 1/r^3$ and the interaction energy is proportional to $1/r^6$. A more complete quantum mechanical argument shows that the potential energy of the two atoms is

$$U = -A\frac{V_1 V_2}{V_1 + V_2}\alpha_1\alpha_2\frac{1}{r^6} \quad \text{A positive constant} \quad (7.1)$$

where V_1, V_2 are the ionization potentials of the two atoms and α_1, α_2 are the polarizabilities. (7.1) ignores the energy of the repulsive forces due to the 'overlap' of the atoms but these are of very short range and consequently the van der Waal energy is much greater than the repulsive energy at the observed intermolecular distance. To find the crystal energy, (7.1) may be summed over all pairs of atoms but this is not difficult as the potential falls off rapidly. (Clearly an approximation is involved as the energy is not strictly a sum of two-body interactions.) The results obtained using the observed values of V_i, α_i and r are in quite good agreement with experiment.

§ 7.3 Hydrogen-bonded crystals

These crystals are weakly bound. A neutral hydrogen atom has only one electron and as expected it normally forms a covalent bond with one other atom. However, this is not always so and

under certain circumstances the hydrogen atom appears to be bonded with two other atoms. This is the hydrogen bond. The other atoms involved are electronegative (such as oxygen, fluorine, etc.) and it is believed that the hydrogen atom loses its electron to one of these. The proton then forms the bond
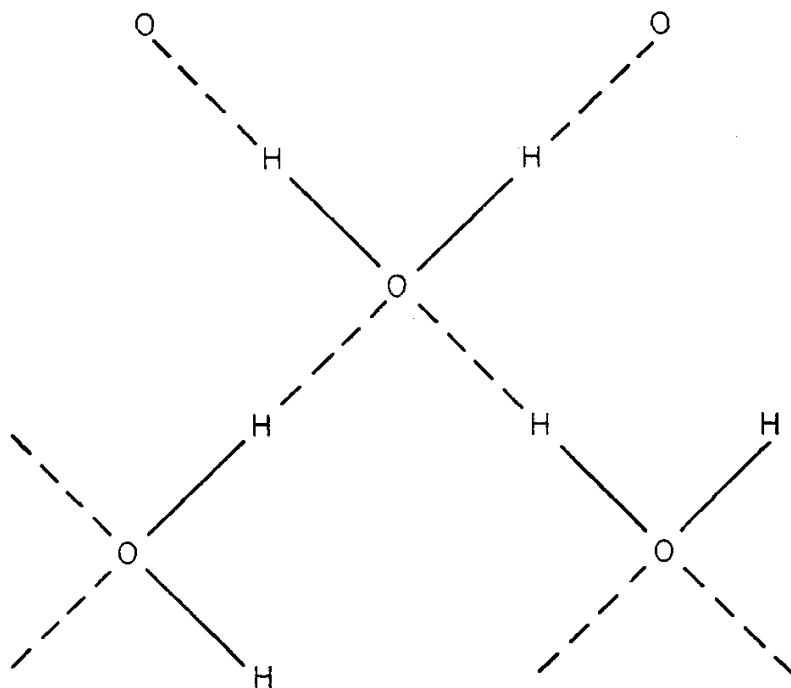
FIG. 7.1   Hydrogen bond, ice

which is mainly ionic but partly van der Waal in character. A notable example of this type of bond occurs in ice where the water molecules are bound to each other by hydrogen bonds.

§ 7.4 Ionic crystals

Ionic crystals are strongly bound with binding energies of about 5–10 eV per molecule. (This is the energy to dissociate the lattice into positive and negative ions at infinite separation.) In the classical Born–Madelung theory of ionic solids it is assumed that the electrons are transferred from electropositive

atoms (e.g. Na, K, Ca) to electronegative atoms (e.g. O, F, Cl). In the model case each ion is taken to possess a charge which is a multiple of the electron charge and has a closed shell structure with spherical symmetry. This is probably a reasonable approximation to the alkali halides. For example sodium chloride may be regarded as composed of positive sodium ions with a neon electron configuration together with negative chlorine ions with an argon electron structure. The overlap between the ions is small and so there is a large gap between the filled and empty electron bands. This explains why sodium chloride is an insulator.

The ions are arranged in the lattice so that the Coulomb attractive force between unlike ions exceeds the repulsion between like ions. It is well-known that no stationary configuration of charges can be in stable equilibrium under their own electrostatic forces (Earnshaw's theorem). The additional force (as in the case of molecular crystals) is the quantum mechanical short range repulsion between the ions which opposes the overlap of the electron distributions. Of course there are other forces as well, such as the van der Waal forces and also the van der Waal type forces produced by the polarization of the ions by the charges on the other ions. These are not two-body interactions and are more difficult to deal with, but fortunately their effects are small. In the latter case the symmetry of the lattice makes the field due to the neighbours cancel to a large extent and in particular the field vanishes at the centre of the ions.

Within the two-body interaction approximation the total crystal potential energy is

$$U = \sum_{i>j} \sum_{j} U_{ij} \qquad (7.2)$$

where U_{ij} is the interaction energy between the i and j ions and the sum includes all pairs. The short range repulsion term is due to the overlap of the ion structures and may sensibly be represented by $\lambda e^{-r_{ij}/\rho}$ where λ, ρ are constants and r_{ij} is the distance

between the ions. (Originally the interaction energy was taken as $Ar_{ij}{}^{-n}$ with $n \sim 10$.)

$$U_{ij} = \pm \frac{(-1)e^2}{4\pi\epsilon_0 r_{ij}} + \lambda e^{-r_{ij}/\rho} \qquad (7.3)$$

e is the magnitude of the charge on each ion and the positive and negative signs are taken for unlike and like charges respectively. If the crystal contains N molecules each with two ions then ignoring surface effects the electrostatic contribution to the total energy is obtained by summing the first term in (7.3) and is

$$-\frac{Ne^2}{4\pi\epsilon_0 r}\alpha \qquad (7.4)$$

r is some lattice parameter and may be taken to be the nearest neighbour distance. α is a positive number called the Madelung constant.

$$\alpha = \sum_{j \neq i} \pm \frac{r}{r_{ij}} \qquad (7.5)$$

α does not depend upon the lattice distance but only upon the crystal structure. A typical value is $\alpha = 1.7476$ as for the NaCl structure. The summation (7.5) is only conditionally convergent and the arrangement of terms is important. This is a consequence of the long range characteristic of the Coulomb force law. The interested reader is referred to the methods of Evjen (1932) and Ewald (1921).

The exponential term in (7.3) falls off rapidly and is only important for nearest neighbours. This non-Coulombic contribution to the total energy is

$$NM\lambda e^{-r/\rho} \qquad (7.6)$$

where M is the co-ordination number ($M = 6$ for NaCl). With this approximation the total lattice potential energy is

$$U = N\left[-\frac{e^2}{4\pi\epsilon_0 r}\alpha + M\lambda e^{-r/\rho} \right] \qquad (7.7)$$

The quantity in brackets is the cohesive energy per molecule. This expression for U contains three parameters r, λ and ρ. At the equilibrium separation $\frac{\partial U}{\partial r} = 0$. This condition may be used to eliminate λ and writing $r = r_0$

$$U = -\frac{Ne^2\alpha}{4\pi\epsilon_0 r_0}\left[1 - \frac{\rho}{r_0}\right] \qquad (7.8)$$

For a given crystal α and r_0 are known and so it remains only to find ρ. This is done indirectly by extrapolating the observed compressibility to absolute zero. The compressibility β is defined by

$$\frac{1}{\beta} = -V\frac{dP}{dV} \qquad (7.9)$$

where P and V are the pressure and crystal volume respectively. From the first law of thermodynamics

$$\delta U = \delta Q - P\,dV$$

and at very low temperatures $\delta Q \sim 0$ and

$$\delta U \simeq -P\,dV \qquad (7.10)$$

The compressibility at absolute zero is then

$$\frac{1}{\beta_0} = V\frac{d^2U}{dV^2} \qquad (7.11)$$

The crystal volume V is equal to the number of ions multiplied by the volume associated with each ion. For NaCl $V = (2N)r^3$ and then from (7.11) and (7.7), after some algebraic manipulation, it is seen that

$$\frac{1}{\beta_0} = \frac{e^2\alpha}{18(4\pi\epsilon_0)r_0^4}\left(-2 + \frac{r_0}{\rho}\right) \qquad (7.12)$$

If β_0 is found from experiment then the ratio ρ/r_0 can be calculated and used in (7.8) to calculate the lattice potential energy. This value may then be compared with the observed

cohesive energy and provides a check on the theory. For the alkali halides $\rho/r_0 \sim 1/10$ and in this case

$$U \simeq -\frac{Ne^2\alpha}{4\pi\epsilon_0 r_0} \cdot \frac{9}{10} \qquad (7.13)$$

The lattice energy is equal to about 0·9 of the Madelung electrostatic energy. For NaCl this is about 8·5 eV per molecule and is in good agreement with experiment.

The Born–Madelung model described above gives the lattice energy as composed of two terms. Fröman and Löwdin (1962) have pointed out that this is not correct and that the total energy involves several terms of the same order as the Madelung energy. Briefly their argument is as follows.

The virial theorem states that in a conservative system in equilibrium, if the potential is a homogeneous function of the co-ordinates of degree n then the average total potential energy V is

$$V = \frac{2}{n}T \qquad (7.14)$$

where T is the average total kinetic energy. (This theorem holds in both quantum and classical mechanics.) For a system where the inter-particle forces are Coulombic $n = -1$ and

$$V = -2T \qquad (7.15)$$

The total energy is then

$$\begin{aligned} T + V &= -T \\ &= \frac{V}{2} \end{aligned} \qquad (7.16)$$

In a many-body quantum mechanical treatment of ionic crystals the potential is Coulombic and the virial theorem is satisfied both for the free ions at infinite separation and for the crystal. The cohesive energy is

$$U = \delta T + \delta V \qquad (7.17)$$

where δT and δV are the changes in the expectation values of

the kinetic and potential energies as the crystal is formed. From the virial theorem

$$U = -\delta T = \frac{\delta V}{2} \qquad (7.18)$$

The kinetic energy is increased by an amount equal in magnitude to half the decrease in the potential energy. Fröman and Löwdin have explained this by assuming that the ions are 'excited' in the crystal and possess a greater kinetic energy than the free ions. This is related to the contraction of the ionic electron distribution on crystal formation. As it is well-known that the Madelung energy is close to the cohesive energy the true change in the potential energy must be about twice as large as the Madelung energy. The extra potential energy is due to the 'overlap of the ions'. (So is the kinetic energy.) The final result is that the cohesive energy is essentially equal to the Madelung energy but there are other large terms which cancel.

§ 7.5 Valence crystals

Valence crystals are very strongly bound with high melting points. Diamond is a good example. When two atoms are brought together their interaction brings about a deformation of the original atomic charge distribution. Bonding between similar or identical atoms may occur if negative charge is transferred from the atoms to the space between them. The two positive 'atoms' are held together by the negative electron space charge. This is the covalent bond. Of course confinement of electron charge in the bond leads to an increase in the kinetic energy which tends to reduce the binding energy. If the decrease in potential energy is greater than the increase in kinetic energy binding will result. According to the virial theorem, when such a stationary state exists the increase in kinetic energy is equal to half the decrease in potential energy. (Note that the kinetic energy has a maximum value in the lowest energy state.)

In a crystal, the total binding energy will not only include the energy within a bond but also the interactions between different bonds. However in many cases the crystal energy is quite close to the sum of the bond energies and this is particularly true for diamond. The C–C bond has a strength of about 3·6 eV in diamond and in organic molecules. This suggests that a study of a single covalent bond would be useful.

Hydrogen-molecular ion H_2^+

This is the simplest type of molecular structure and illustrates the essential effects of the covalent bond in that two hydrogen nuclei are held together by a negative charge between them. Within the Born–Oppenheimer approximation this is a single particle problem, the two nuclei being in fixed positions. If the protons are a distance R apart the Hamiltonian is

$$\mathscr{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_0}\left(\frac{e^2}{r_1} + \frac{e^2}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0 R} \quad (7.19)$$

where r_1, r_2 are the distances of the electron from the two protons.

The electron wave function satisfies the equation

$$\mathscr{H}\psi = E(R)\psi \quad (7.20)$$
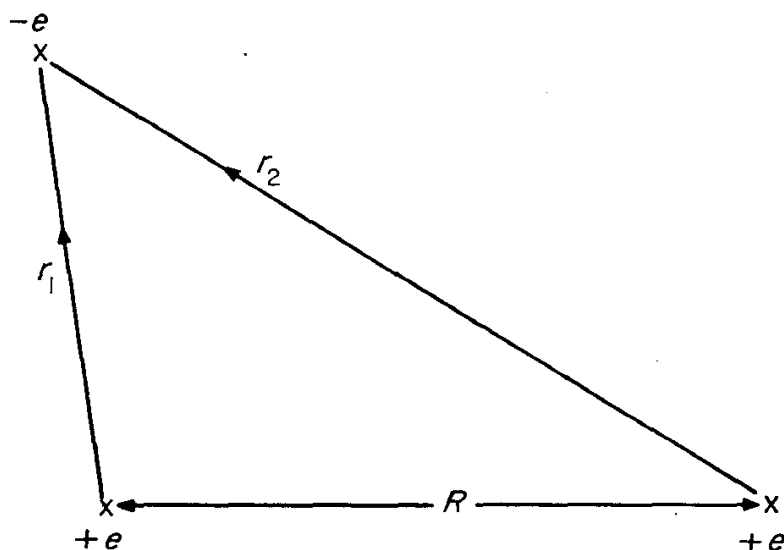
FIG. 7.2   Hydrogen-molecular ion

and the energy of the system may be found for a given R. Equation (7.20) can be solved exactly in elliptic co-ordinates and the energy found for different values of R.
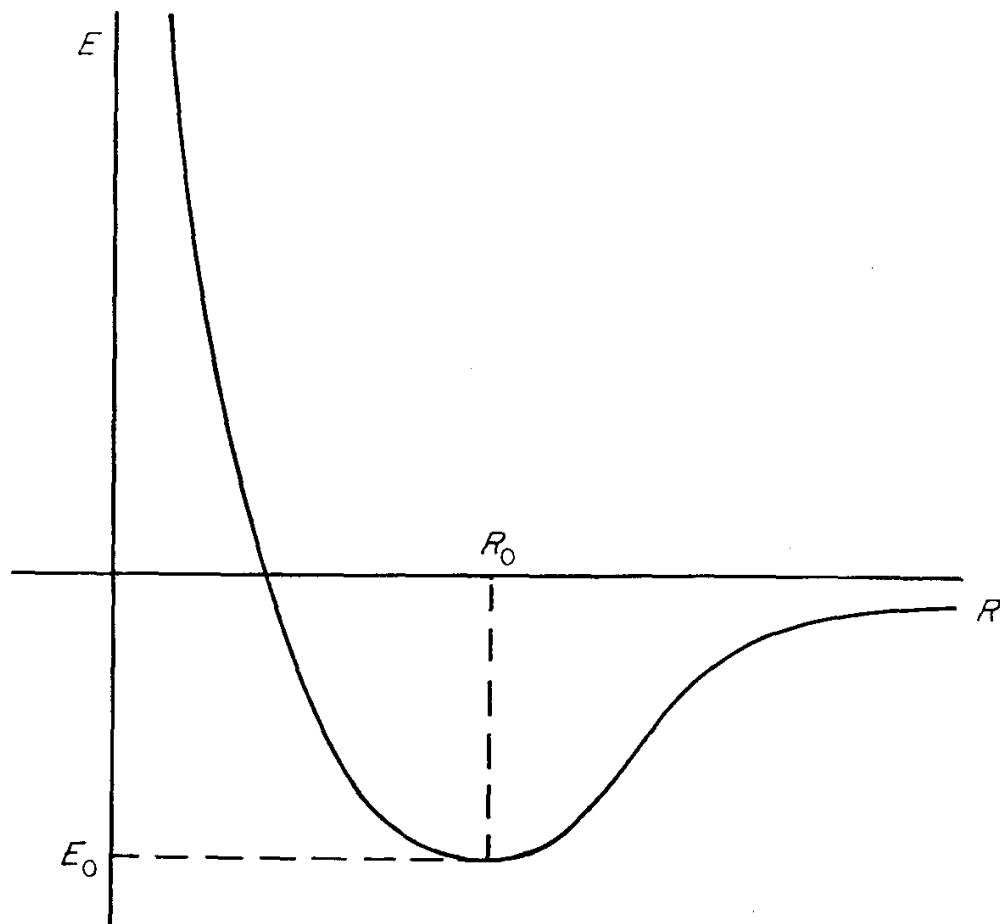
FIG. 7.3   Minimum of E gives stable separation

The turning point on the $E(R)$ curve defines the equilibrium separation of the protons.

Calculation predicts the separation to be 1·06 Å in agreement with experiment. The wave functions may be classified by their components of orbital angular momentum about the bond axis and it is found that the lowest stable state has an axially symmetric σ wave function with zero angular momentum. To find the cohesive energy of the molecule it is necessary to subtract from the minimum E_0 the energy of a proton and hydrogen

atom (in its lowest state) at infinite separation. (This is 1 Rydberg $\simeq$ 13·5 eV.) The binding energy is found to be almost 2·8 eV again in good agreement with experiment.

A less exact but still useful approach is to obtain the molecular orbital as a linear combination of atomic orbitals (L.C.A.O.). The simplest approximation to the ground state would be to set the molecular orbital

$$\psi = C_1\psi_1 + C_2\psi_2 \qquad (7.21)$$

where ψ_1, ψ_2 are the real normalized hydrogen ($1s$) wave functions centred on the two protons. The symmetry group of the Hamiltonian is the infinite group ∞/mm. This group includes the inversion through the centre of the bond and for a non-degenerate state $C_2 = \pm C_1$. The two wave functions are

$$\psi_g = C_1(\psi_1 + \psi_2) \qquad \text{gerade (even)}$$
$$\psi_u = C_1'(\psi_1 - \psi_2) \qquad \text{ungerade (odd)}$$

C_1 and C_1' are determined by normalizing the molecular wave functions. The corresponding energies are obtained from

$$E = \frac{\int \psi^* \mathscr{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

i.e.
$$E_g = (\mathscr{H}_{11} + \mathscr{H}_{12})/(1 + S) \qquad (7.22)$$
$$E_u = (\mathscr{H}_{11} - \mathscr{H}_{12})/(1 - S)$$

where

$$\mathscr{H}_{ij} = \int \psi_i^* \mathscr{H} \psi_j \, d\tau \qquad (7.23)$$

and S is the real overlap integral

$$S = \int \psi_1^* \psi_2 \, d\tau$$

S is considerably less than unity and

$$E_g \simeq \mathscr{H}_{11} + \mathscr{H}_{12} \qquad (7.24)$$
$$E_u \simeq \mathscr{H}_{11} - \mathscr{H}_{12}$$

Bonding state

Antibonding state
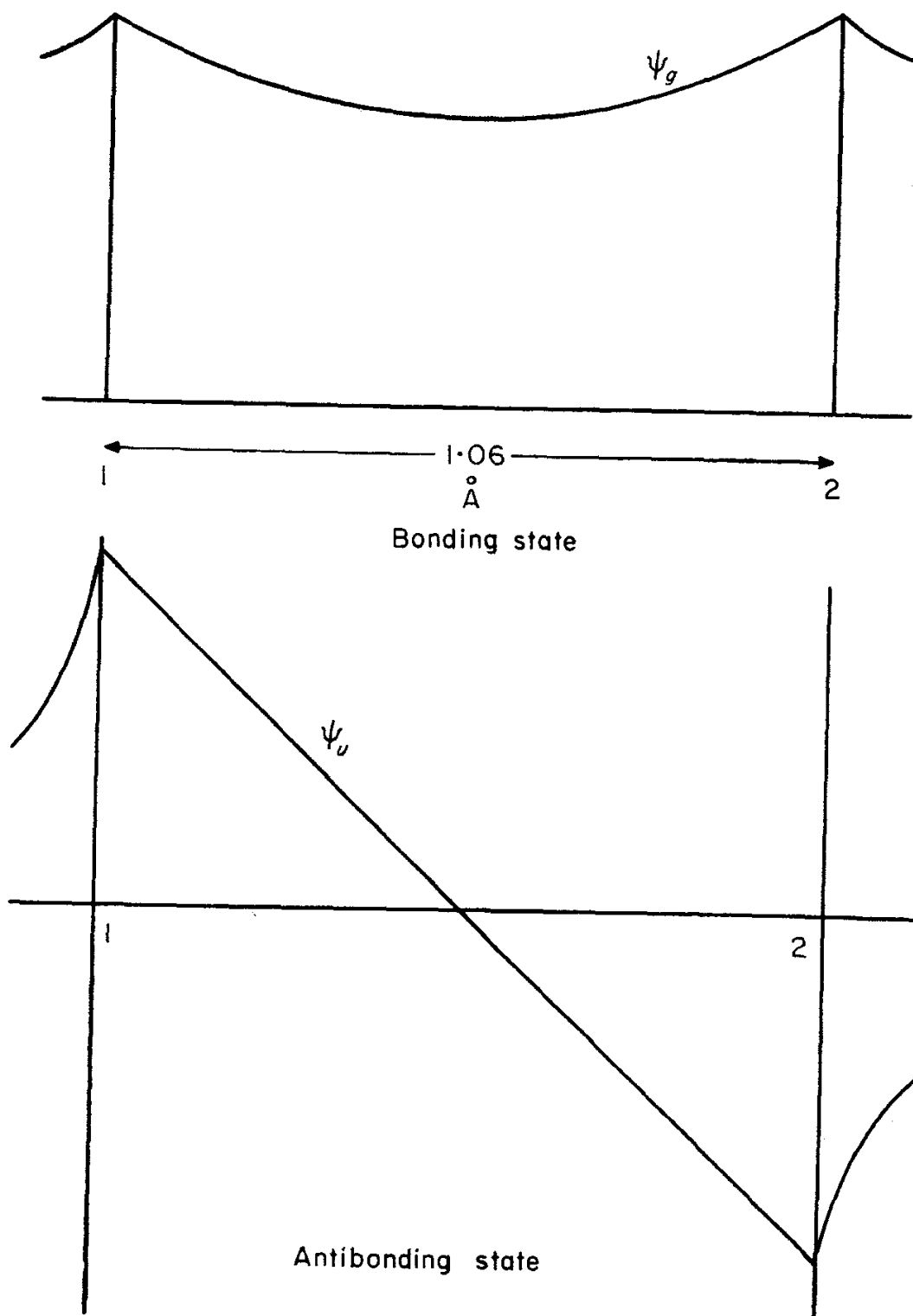
Fig. 7.4

As ψ_1 and ψ_2 are both positive in the region of overlap then it can be shown that $\mathscr{H}_{12} < 0$ and the lowest energy state is the 'gerade' state with the symmetric wave function. In general it is true that the more overlap there is between the atomic orbitals the lower the energy will be for the gerade state and the stronger the bond will be. The lowest energy state is often called the bonding state and the charge density is

$$| \psi_g |^2 = C_1^2(\psi_1^2 + \psi_2^2 + 2\psi_1\psi_2) \qquad (7.25)$$

The term $2\psi_1\psi_2$ represents the bond charge. Compare this with the charge density from the ungerade (anti-bonding) state where charge is removed from the bond.

$$| \psi_u |^2 = C_1'^2(\psi_1^2 + \psi_2^2 - 2\psi_1\psi_2) \qquad (7.26)$$

With the hydrogen ($1s$) states the binding energy is calculated to be $\sim 1\cdot 8$ eV which involves an error of 1 eV. A considerable improvement is obtained if some parameter, such as effective nuclear charge, is included in the wave functions and varied to minimize the energy.

The hydrogen molecule H_2

This is the simplest molecule involving more than one electron but even so no exact solution exists. The hydrogen ion bond wave function should be able to take up another electron with opposite spin and result in a stable state. The energy with the electron pair in the bonding orbital will be lower than that of two hydrogen atoms at infinite separation. Certainly the binding energy of the hydrogen molecule will be greater than that of the hydrogen ion but not twice as large because of the repulsion between the electrons. These predictions are confirmed by experiment and the binding energy is found to be $4\cdot 7$ eV.

The simple molecular orbital method does not give good agreement with experiment. In this model both electrons are taken to be in the hydrogen ion bonding state with opposite spins and the two-electron wave function is

$$\psi_g(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_g(1)\alpha(1) & \psi_g(1)\beta(1) \\ \psi_g(2)\alpha(2) & \psi_g(2)\beta(2) \end{vmatrix} \qquad (7.27)$$

$$= \frac{1}{\sqrt{2}} \psi_g(1)\psi_g(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

The spacial part may be expanded to give

$$\psi_g(1)\psi_g(2) = C_1{}^2[\psi_1(1)\psi_1(2) + \psi_2(1)\psi_2(2) \\ + \psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)] \quad (7.28)$$

The wave function gives equal weight to the ionic states of the type $\psi_1(1)\psi_1(2)$ where the two electrons are on the same atom and to the remaining states in which each atom has one electron. Energetically it is clear that the ionic states should not be as important as this wave function suggests. The electrons tend to keep apart and this may be taken into account by configuration interaction in which the two-electron wave function is expressed as a linear combination of determinants. Group theoretical considerations indicate that the lowest determinantal wave function which will mix in is that obtained by exciting both electrons to the antibonding orbital. This wave function is

$$\psi_u(r_1\ r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_u(1)\alpha(1) & \psi_u(1)\beta(1) \\ \psi_u(2)\alpha(2) & \psi_u(2)\beta(2) \end{vmatrix} \qquad (7.29)$$

with spacial part

$$\psi_u(1)\psi_u(2) = C_1'{}^2[\psi_1(1)\psi_1(2) + \psi_2(1)\psi_2(2) \\ - \psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(1)] \quad (7.30)$$

By taking a suitable combination of (7.27) and (7.29) the ionic terms may be reduced or eliminated. When the energy is minimized in this way, the combination is such that the ionic terms are relatively unimportant.

Clearly then, a better first wave function (instead of (7.27)) would be to take the electrons on different atoms to begin with. This is the basis of the Heitler–London approach where the spacial part of the wave function is approximated by $[\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)]$. Some electron correlation is built

in already in this method and the energy is minimized by varying parameters in ψ_1 and ψ_2. This method is obviously correct in the limit as $R \longrightarrow \infty$ as the electrons are then indeed on different atoms. This Heitler–London wave function and the best two-determinant molecular orbital wave function are of equivalent accuracy and both involve an error of about 0·5 eV.

Extension to crystals

The physics of the covalent bond is illustrated by H_2^+ and H_2 and the insight gained by the study of these two molecules may be used to tackle the much more difficult crystal problem. In a covalent crystal there are electron-pair bonds between the atoms, one electron being donated by each atom. (The Pauli principle does not permit a third electron in a bonding orbital.) Essentially the energy of a bond depends upon the overlap between the atomic orbitals on the different atoms. It is often possible to increase the overlap by mixing the atomic orbitals to form hybridized wave functions which are localized along the bond. A classic example is given by the carbon atom.

The free carbon atom in the ground state has the electron configuration $(1s)^2(2s)^2(2p)^2$. It is well known that the carbon atoms in molecules or crystals often have a tetrahedral environment (e.g. methane, diamond). This implies that there are four unpaired electrons available for bond formation. This quadrivalent property may be explained if it is assumed that in the 'valence state' one of the $(2s)$ electrons is excited to a $(2p)$ state to give the configuration $(1s)^2(2s)(2p)^3$. From the four valence state electrons it is possible to construct four directed hybrid orbital by a unitary transformation.

These may be chosen to have their maxima in the four directions $(1\ 1\ 1)$, $(\bar{1}\ \bar{1}\ 1)$, $(1\ \bar{1}\ \bar{1})$ and $(\bar{1}\ 1\ \bar{1})$. Each hybrid has the form

$$t_{111} = \tfrac{1}{2}(s + \sqrt{3}p_{111}) \tag{7.31}$$

with $$p_{111} = \frac{1}{\sqrt{3}}(p_x + p_y + p_z)$$
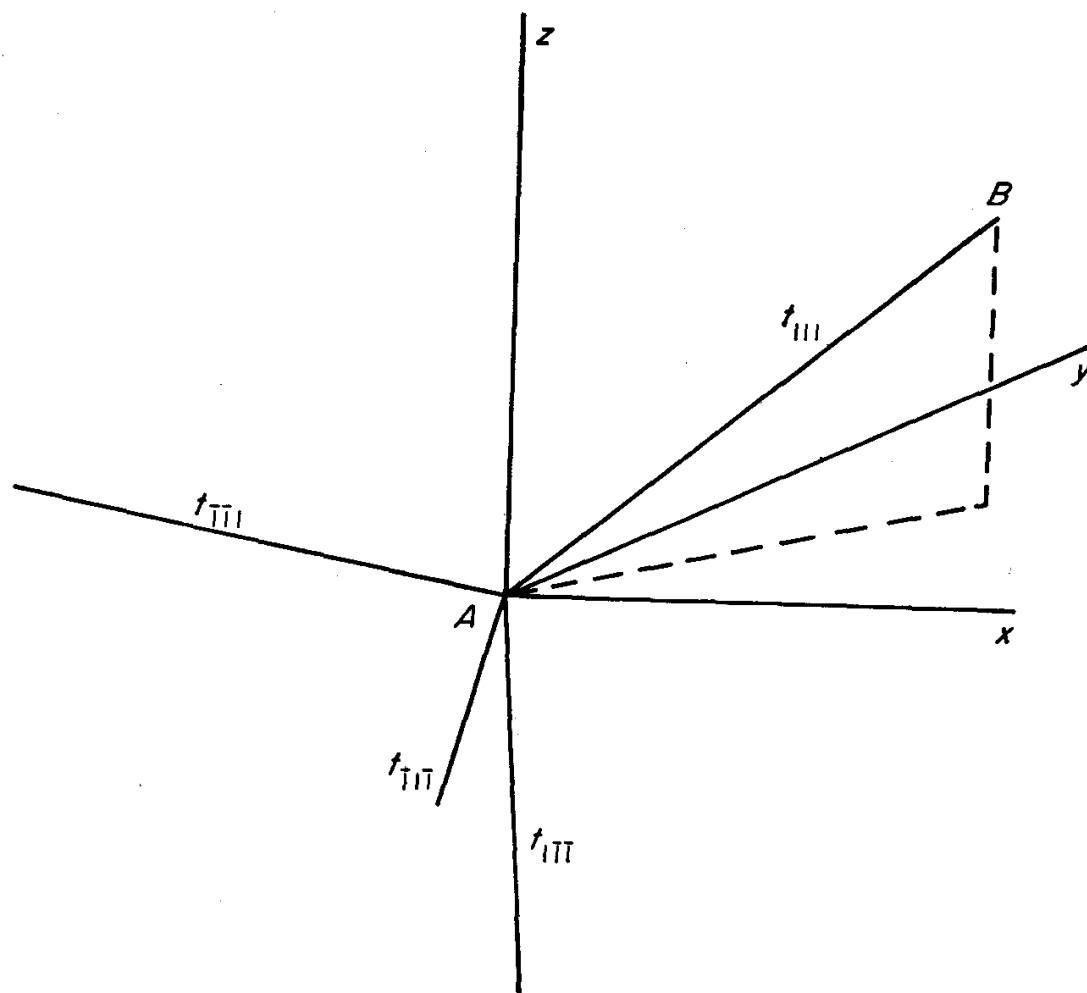
FIG. 7.5

By analogy with the hydrogen molecule, a bond orbital $\chi(\mathbf{r})$ may be constructed between two carbon atoms A and B.

i.e.
$$\chi(\mathbf{r}) = \frac{1}{\sqrt{2(1+S)}}(t_A + t_B) \qquad (7.32)$$

where t_A is the hybrid orbital on site A pointing towards the nearest neighbour B and S is the overlap integral. The gain in energy on bond formation more than compensates for the energy required to excite the valence state.

These intuitive ideas can be formalized by a band theoretic approach. In Chapter 5 it was shown how a non-degenerate band can be described by a set of orthogonal localized orbitals.

P

Each Bloch function can be expressed as a linear combination of these Wannier functions. There is one Wannier function per primitive cell. In the same way it can be shown that a set of degenerate bands may be described by a set of orthogonal localized orbitals which are identical apart from their location and/or orientation in space. If the bands are completely occupied these orbitals are called equivalent orbitals, otherwise they are referred to as site orbitals. For diamond there are four filled valence bands corresponding to the atomic states $(2s)(2p)^3$. These bands are degenerate at certain points in the Brillouin zone and it can be shown that the equivalent orbitals may be chosen to be centred on the bonds between the carbon atoms, there being four in each primitive cell (Hall, 1952, 1958).

In a first approximation the many-electron wave function is written either as a determinant whose elements include all the occupied Bloch functions or whose elements are the equivalent orbitals. These are identical, but it is often preferable to work in terms of localized functions. Configuration interaction may be conveniently introduced by mixing in other determinantal wave functions in which one or both electrons in a bond are excited. Work by Schmid (1953) on the cohesive energy of diamond suggests that a single determinant of bond equivalent orbitals is a reasonable approximation. The configuration interaction which is so important in the hydrogen molecule does not play such a decisive part in diamond.

§ 7.6 Metals

The attempts to calculate metal cohesive energies are somewhat different in approach than those used for covalent crystals. In valence crystals it has proved useful to introduce the equivalent orbitals, there being one equivalent orbital for each bond. This method is not very appropriate for metals as the number of equivalent orbitals is less than the number of bonds. Metallic sodium crystallizes in the b.c.c. lattice with eight nearest neigh-

bours demanding four bonds per primitive cell. Sodium has one 'free' electron and the valence band is only half-filled in the lowest energy state. It is possible to form localized equivalent orbitals by taking linear combinations of the Bloch functions of the lower half of the band, but there is only one such orbital for every two primitive cells. These orbitals are not as localized as those obtained for covalent crystals. Clearly it is impossible to give these equivalent orbitals the same significance as in the case of covalent structures.

In practice it has proved more fruitful to recognize the similarities between metal electrons and free electrons in cohesive energy calculations. This is not to say that the metallic bond is of a completely different nature. There is certainly a covalent effect in that there is a movement of charge into the space between atoms.

Cellular method

The first steps in a cohesive energy calculation is to find an accurate solution to the single electron problem. Wigner and Seitz (1933, 1934) introduced the cellular method to do this for the lowest energy state in monovalent alkali metals. This method was briefly mentioned in Chapter 5 where it was pointed out that the approach is completely different from the plane wave and tight-binding method. An attempt is made to find as accurate a solution as possible in the region of the ion cores and then the lattice periodicity is imposed as a boundary condition.

Real space may be divided into space-filling cells in the same way that the reciprocal lattice is divided into Brillouin zones. Each lattice point is surrounded by such a Wigner–Seitz cell formed by the planes bisecting the lines joining the point to its neighbours. For crystals with b.c.c. direct lattices (e.g. sodium) the Wigner–Seitz cell is a truncated regular octahedron with fourteen faces.

The potential at a point inside a cell may be divided into two parts, that arising from within and that arising from outside the

cell. Again, there are two contributions to the potential from within the cell. Firstly, there is the effect of the ion core. This has a spherically symmetrical closed shell and the potential may be approximated by some analytic representation of the free ion potential. Secondly, there is the potential arising from the smoothed out charge distribution of all the other valence electrons within the cell. This may be neglected in a first approximation. The potential from outside the cell is due to the other ion cores and valence charge not included in the cell. Symmetry requires that each cell be electrically neutral. It is consistent to assume that all cells are almost spherically symmetric and so the potential outside an isolated cell is very small and may be neglected. The potential V inside any cell may be taken to be entirely due to the spherical ion core within.

In a simple treatment the cell is replaced by a sphere of equal volume. The lowest state ($k = 0$) of the valence band has the same symmetry as the atomic functions from which it is derived. In sodium, the valence band is derived from the ($3s$) state. The wave equation is separable in the co-ordinates and the radial part of the wave function $R(r)$ satisfies the equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2m}{\hbar^2}[E(0) - V]R = 0 \qquad (7.33)$$

The allowed energies $E(0)$ are determined by the boundary conditions imposed which are that the wave function and its derivative must be continuous at the cell boundary and also satisfy the Bloch condition. In the case considered

$$\left(\frac{dR}{dr}\right)_{r_0} = 0 \qquad (7.34)$$

where r_0 is the radius of the Wigner–Seitz sphere. In addition $R(r)$ must have two spherical nodes as it must resemble the ($3s$) state near the ion. The values of $E(0)$ corresponding to different values of r_0 may be calculated. At the observed lattice spacing, the energy obtained from the boundary condition (7.34) is considerably lower than that for a free atom and is the

main cause of binding in metals. Wigner called this the 'boundary correction'. Of course it is not possible for all the electrons to be simultaneously in the state $k = 0$. If an effective mass m^* may be assumed then the energies of the higher states are

$$E(k) = E(0) + \frac{\hbar^2 k^2}{2m^*} \qquad (7.35)$$

For the alkali metals it may be shown that the electrons behave as if they were almost free and it is reasonable to take $m^* \sim m$.

When the potential arising from all the other valence electrons inside the cell is ignored then in effect some electron correlation is introduced as it implies there is only one electron inside the cell at any given moment. The crystal energy is essentially the sum $\sum E(k)$ of the energies of the electrons in the field of their own ion cores. All the other electron–ion, electron–electron and ion–ion interactions in the Hamiltonian 1.10 cancel in this approximation. It is not difficult to show that the average electron energy is

$$\bar{E} = E(0) + E_B \qquad (7.36)$$

with $$E_B = \frac{3}{5} \frac{\hbar^2 k^2_m}{2m^*}$$

where k_m is the wave vector for the highest occupied state. The binding energy is then

$$E(A) - [E(0) + E_B] \qquad (7.37)$$

where $E(A)$ is the free atom energy. For sodium the boundary correction $E(A) - E(0)$ is about 3 eV and for a half-filled band the mean band energy $E_B \sim 2$ eV. The binding energy is ~ 1 eV in quite good agreement with experiment. For a full band the band energy would just about cancel the boundary correction and there would be no binding.

The above is a greatly simplified treatment of the problem. If the smoothed-out electron distribution inside the sphere is not neglected (Problem 8) then it can be shown that the energy of the crystal is increased and becomes greater than that of the

free atoms and so there is no binding. This somewhat surprising result is due to the fact that the correlation originally incorporated by ignoring this term has been removed. However, if correlation is reintroduced in a more consistent manner it may be shown that the correlation energy more or less cancels the smoothed electron term, so restoring binding. For this purpose Wigner and Seitz considered a gas of free electrons of the same density as the metallic electrons but these modifications are beyond the scope of this book.

In the method described above the result depends upon the atomic volume and not upon the crystal structure. Refinements have been introduced by retaining the Wigner–Seitz polyhedron and fitting a wave function to satisfy the boundary conditions at a selected number of points on the surface.

Metals are plastic solids as the binding forces are essentially non-directional. On the other hand the directional character of the bonds in covalent solids resist shear and consequently covalent solids are brittle.

Problems for Chapter 7

1. Consider an infinite line of ions spaced a distance a apart. The ions have charges of equal magnitude but alternate in sign. Show that relative to the nearest neighbour distance the Madelung constant has the value 2 ln 2.

2. In the text the short-range repulsion term between the i and j ions is taken to be $\lambda e^{-r_{ij}/\rho}$. The early workers took this interaction to be Ar_{ij}^{-n} where A, n are constants. Show that a value of $n \sim 10$ is consistent with equation (7.13).

3. In free space the flux of the electric field $\mathscr{E}$ out of a closed surface S is

$$\oint_S \mathscr{E} \cdot \mathrm{d}S = \frac{q}{\epsilon_0}$$

where q is the included charge and ϵ_0 is the permittivity of free

space. The scalar potential ϕ is defined to within an arbitrary constant by $\mathscr{E} = -\text{grad } \phi$. Show that ϕ can not have a maximum or minimum value except at points where there is a positive or negative charge respectively. Deduce that a free charge can not be in stable equilibrium at a point unoccupied by charge. This result implies that no stationary arrangement of charges can be in stable equilibrium under their own influence.

4. In the discussion of the hydrogen molecular ion $\mathscr{H}_{ij}$ was defined by equation (7.23). Show that

$$\mathscr{H}_{12} = \left(E_H + \frac{e^2}{4\pi\epsilon_0 R}\right)S - \int \psi_1 \frac{e^2}{4\pi\epsilon_0 r_1}\psi_2 \, d\tau$$

and

$$\mathscr{H}_{11} = \left(E_H + \frac{e^2}{4\pi\epsilon_0 R}\right) - \int \psi_1 \frac{e^2}{4\pi\epsilon_0 r_2}\psi_1 \, d\tau$$

where E_H is the hydrogen atom eigenvalue for the $(1s)$ state. A similar result holds for $\mathscr{H}_{22}$. Using equation (7.24) derive the expression

$$E_g = E_H + \frac{e^2}{4\pi\epsilon_0 R} - \int \frac{e^2}{4\pi\epsilon_0 r_2}\psi_1^2 \, d\tau - \int \frac{e^2}{4\pi\epsilon_0 r_1}\psi_1\psi_2 \, d\tau$$

and also the expression for E_u. Explain why $E_g < E_u$ and state why this implies that $\mathscr{H}_{12} < 0$.

5. Suppose a system of classical particles is in motion. Newton's second law states that $X_i = m_i \ddot{x}_i$ where X_i is the force in the x-direction acting on the ith particle of mass m_i. Confirm the expression

$$\frac{x_i}{2}X_i = -\frac{m_i}{2}\dot{x}_i^2 + \tfrac{1}{2}\frac{d}{dt}(m_i x_i \dot{x}_i)$$

Show that provided the particle is confined to a finite region of space, the time average as $t \longrightarrow \infty$ of the last term on the r.h.s. is zero. For conservative systems the forces acting on the particles may be derived from a scalar potential.

$$X_i = -\frac{\partial}{\partial x_i}V(x_1, y_1, z_1, \ldots)$$

If V is a homogeneous function of the co-ordinates of degree n show that

$$\frac{n}{2}\bar{V} = \bar{T}$$

where $\bar{V}$ and $\bar{T}$ are the time averages of the potential and kinetic energies of the system as $t \longrightarrow \infty$. (You may use Euler's theorem $\sum_i \left(x_i \frac{\partial V}{\partial x_i} + y_i \frac{\partial V}{\partial y_i} + z_i \frac{\partial V}{\partial z_i} \right) = nV$.) This is the virial theorem for classical mechanics.

6. A classical particle of mass m undergoes harmonic oscillations with angular frequency ω. Show that the potential energy at any point in the path is $m\omega^2 x^2/2$. Hence show that the time average of the potential energy taken over one period is equal to the time average of the kinetic energy. Explain how this result is in accordance with the virial theorem.

7. A hybrid orbital ψ is to be formed from the functions $(2s)$, $(2p_x)$, $(2p_y)$ and $(2p_z)$.

i.e. $\psi = f(r)[a + \sqrt{3}(b\cos\theta + c\sin\theta\cos\phi$
$$+ d\sin\theta\sin\phi)]$$

r, θ, ϕ are spherical polar co-ordinates, a, b, c, d are constants. $f(r)$ is a radial function. The directions in which ψ has a maximum value may be obtained by putting $\frac{\partial\psi}{\partial\phi} = \frac{\partial\psi}{\partial\theta} = 0$. Show that the value of the orbital in the maximum direction (orbital strength) is

$$S = f(r)[a + \sqrt{3(b^2 + c^2 + d^2)}]$$

If ψ is normalized to unity $1 = a^2 + b^2 + c^2 + d^2$. Show that for a pure $(2s)$ orbital $S = f(r)$ and for a pure $(2p)$ orbital $S = \sqrt{3}f(r)$. The maximum possible strength of such a hybrid is given by $\frac{dS}{da}(a) = 0$. Confirm that this is obtained when tetrahedral orbitals are constructed (equation (7.31)). (Pauling (1960) has indicated that the 'strength' of a wave function is a

measure of its bond forming power. Murrell (1960) has extended this principle to produce maximum overlap of the hybrids involved in a bond.)

8. The conduction electron wave functions in an alkali metal are sometimes approximated by plane waves $\psi_k = e^{ik \cdot r}/\sqrt{\Omega}$ where Ω is the metal volume. Verify that the charge density ρ is a constant. In the Wigner–Seitz method, the Coulomb potential at a point depends only upon the charge distribution within the sphere that contains the point.

$$\therefore \qquad \phi(r) = \frac{1}{4\pi\epsilon_0} \int_V \frac{\rho(r')}{|r' - r|} \, d\tau$$

V is the volume of the Wigner–Seitz sphere. The electronic charge in each cell is $-e$. Show that the contribution to the potential from the electronic charge is

$$\phi(r) = \frac{-e}{4\pi\epsilon_0} \left[\frac{3}{2} \frac{1}{r_s} - \frac{r^2}{2r_s^3} \right]$$

where r_s is the radius of the sphere. Explain why this smoothed out charge adds a contribution

$$\tfrac{1}{2} \int_V (-e\phi) \, d\tau/V$$

to the metallic cohesive energy. (Note the factor $\tfrac{1}{2}$.) Verify that this addition to the energy is $0.6e^2/4\pi\epsilon_0 r_s$. (This extra term gives the energy in a 'modified' Hartree approximation. Correlation is ignored entirely.)

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Solutions to Problems

Chapter 1

6. $H = \dfrac{p^2}{2m} + \dfrac{e}{2m}(p \cdot A + A \cdot p) + \dfrac{e^2}{2m} A^2 - e\phi$

$\mathscr{H} = -\dfrac{\hbar^2}{2m} \nabla^2 - \dfrac{e}{m} i\hbar A \cdot \mathrm{grad} - \dfrac{e}{2m} i\hbar \, \mathrm{div} \, A + \dfrac{e^2}{2m} A^2 - e\phi$

Chapter 3

5.

$2mm$	E	2_z	m_y	m_x
E	E	2_z	m_y	m_x
2_z	2_z	E	m_x	m_y
m_y	m_y	m_x	E	2_z
m_x	m_x	m_y	2_z	E

6.

$3m$	E	3_z	3_{z^2}	m_1	m_2	m_3
E	E	3_z	3_{z^2}	m_1	m_2	m_3
3_z	3_z	3_{z^2}	E	m_3	m_1	m_2
3_{z^2}	3_{z^2}	E	3_z	m_2	m_3	m_1
m_1	m_1	m_2	m_3	E	3_z	3_{z^2}
m_2	m_2	m_3	m_1	3_{z^2}	E	3_z
m_3	m_3	m_1	m_2	3_z	3_{z^2}	E

7. As in 6 with

$$(1\ 2\ 3) \sim \mathrm{E} \qquad (2\ 3\ 1) \sim 3_z \qquad (3\ 1\ 2) \sim 3_{z^2}$$
$$(1\ 3\ 2) \sim m_1 \qquad (3\ 2\ 1) \sim m_2 \qquad (2\ 1\ 3) \sim m_3$$

10. Four one-dimensional irreducible representations.
    Two two-dimensional irreducible representations.
    Four three-dimensional irreducible representations.

11. Two one-dimensional irreducible representations.
    One two-dimensional irreducible representation.
    Two three-dimensional irreducible representations.

13. $f(x) + f(-x), \quad f(x) - f(-x)$.

14. B_2) xy, E) xz, yz.

16. A_1, A_3.

Chapter 4

5. $\Omega/2\pi^2\gamma^3$

Chapter 5

9. $E_2(k) = \frac{1}{2}[H_{11}(1 - \sec\theta) + H_{22}(1 + \sec\theta)]$

$$\Psi_2 = -i\sin\frac{\theta}{2}\,\psi_{1k} - \cos\frac{\theta}{2}\,\psi_{2k}$$

Chapter 6

5. $\bar{\tau}_h = \int_{-\infty}^{0} \tau(E)(-E)^{3/2}\, e^{E/kT}\, \mathrm{d}E \Big/ \int_{-\infty}^{0} (-E)^{3/2} e^{E/kT}\, \mathrm{d}E$

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